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I. *The Resistivity and Conductivity of Dilute Amalgams at various Temperatures.* By T. I. EDWARDS, *M.Sc., Research Student, University College of Swansea* *.

INTRODUCTION.

THE work described in this paper is a continuation of that carried out by E. J. Williams †, who determined accurately the conductivities of mercury, and dilute amalgams of cadmium, indium, and magnesium at temperatures ranging from 0° C. to 300° C.

Although a large number of observations have been carried out by various workers on the conductivities of several amalgams the results are not always in agreement, and, in addition, there are still some amalgams whose conductivities at different temperatures have not been investigated.

The present investigation deals with amalgams of thallium, germanium, antimony, yttrium, cerium, aluminium, and beryllium, and the results are examined in relation to a theory put forward by Skaupy ‡.

It is a well-known experimental fact that the conductivity of liquid mercury is, in general, increased by the addition of even small quantities of metals such as zinc, cadmium, and lead. The results are in marked contrast to those obtained

* Communicated by Prof. E. J. Evans, D.Sc.

† Phil. Mag. Sept. 1925, p. 589.

‡ Skaupy, *Zeit. für Physik. Chemie*, lxviii. p. 560 (1907); *Verhd. Deut. Phys. Ges.* xvi. p. 156 (1914); *Ibid.* xviii. p. 252 (1916); *Phys. Zeit.* xxi. p. 597 (1920).

with homogeneous solid solutions where the conductivity is lowered, and cannot be attributed to the difference between liquid and solid as is shown by the fact that certain dilute alkali amalgams are poorer conductors than pure mercury.

Skaupy bases his theory on an analogy between liquid metals and electrolytic solutions, and assumes that the electrical conductivity of a pure solvent must be expressed as a function of the concentration of electrons and of internal friction.

He further assumes that dilute metallic solutions must show a higher electron concentration than the solvent, as splitting off of electrons occurs when the dissolved substance dissociates, and also that chemical relations of equilibrium must exist between solvent and matter dissolved, as both possess a common ion in the negative electron.

The conductivity L of a metallic liquid is proportional to the electron concentration ϵ, and inversely proportional to the internal friction (viscosity) η, and this can be written

$$\epsilon = \text{constant} \cdot \mathrm{L} \cdot \eta. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Taking logarithms of both sides of the equation and differentiating, we obtain :

$$\frac{1}{\epsilon}\Delta\epsilon = \frac{1}{\mathrm{L}}\Delta\mathrm{L} + \frac{1}{\eta}\Delta\eta. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let c = concentration of substance dissolved in mercury expressed in gram atoms per 100 gram atoms of mercury, *i. e.*, approximately in atom atoms per cent.

Dividing by c, equation (2) becomes

$$\frac{1}{\epsilon}\frac{\Delta\epsilon}{c} = \frac{1}{\mathrm{L}}\frac{\Delta\mathrm{L}}{c} + \frac{1}{\eta}\frac{\Delta\eta}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Δ expresses that we are dealing with finite changes however small, corresponding to small but finite concentrations, and we can substitute for L and η suitable corresponding values for the pure solvent.

Putting

$$\frac{1}{\epsilon}\frac{\Delta\epsilon}{c} = \mathrm{H}\,; \quad \frac{1}{\mathrm{L}}\frac{\Delta\mathrm{L}}{c} = l, \text{ and } \frac{1}{\eta}\frac{\Delta\eta}{c} = r,$$

we obtain from (3)

$$\mathrm{H} = l + r,$$

which for infinite dilution can be expressed as

$$\mathrm{H}_\infty = l_\infty + r_\infty. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Skaupy showed in his first paper that l_∞ has approximately the same value for a number of metals dissolved in mercury.

The rule that l_∞ is approximately constant for different metals does not hold in the case of some alkali amalgams, and the difficulty was not removed until Feninger's * work showed the increased value of the viscosity for these amalgams. If this is taken into account, we obtain the more general rule that

$$H_\infty = l_\infty + r_\infty$$

should have the same order of magnitude for different metals dissolved in mercury.

Another point of interest discussed by Skaupy is the variation of H with concentration. It can be shown that $\frac{H_\infty - H}{c}$ must be constant; but, as the variation of internal friction with increase of concentration is not sufficiently known, one is often obliged to consider the values of $\frac{l_\infty - l}{c}$ in the case of amalgams in which the change of internal friction is not so great as in the alkali metals.

In the present paper the values of l_∞ and $\frac{l_\infty - l}{c} = K$ will be discussed for the amalgams examined.

The metals used in these experiments were supplied by Messrs. Harrington Bros. and were the purest they could procure. In the case of both thallium and cerium, two specimens obtained from different sources were employed and the results were found to be identical. The germanium was obtained from Dr. Schuchardt, Görlitz. It is, however, difficult to be certain about the state of purity of yttrium.

Before the experiments on amalgam were commenced, the work of Williams on the conductivity of mercury at various temperatures from 0° C. to 300° C. was repeated in a quartz tube, so as to minimise as far as possible the corrections that must be applied due to the expansion of the containing vessel.

Experimental Arrangement.

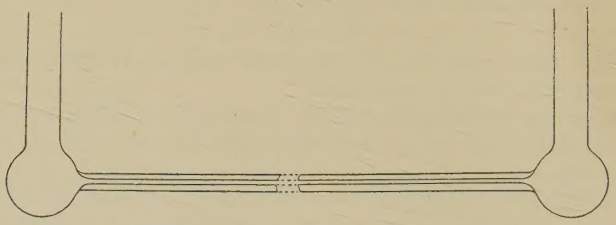
The resistance of a fine column of liquid contained in a capillary tube (as shown in fig. 1) was measured by means of a Callendar and Griffiths Bridge, and a high sensitivity galvanometer which gave a deflexion of 1 mm. on a scale 1½ metre away when a current of $2{\cdot}5 \times 10^{-9}$ ampere was passed through it. With the bridge used the resistance could be estimated to ·00005 ohm, this corresponding to a change of temperature of ·05° C.

The various resistances of the bridge were known in

* H. Feninger, 'Die Electrische Leitfähigkeit und innere Reibung Verdünntner Amalgame,' Freiburg, 1914.

relation to one another, so as to be able to determine the relative changes of the resistances measured. A knowledge of the correct absolute values of the bridge resistances is not necessary for an accurate determination of the temperature

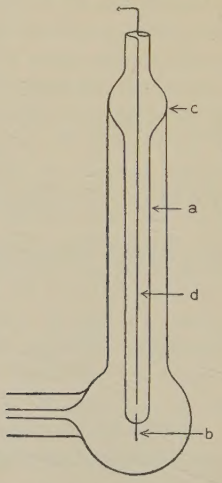
Fig. 1.



coefficient of resistivity of mercury or amalgam, as long as their relative values are known accurately. Even in the case of the absolute determinations of resistivity of mercury and amalgams the absolute value of the bridge resistances is not required as the resistivity of mercury at 0^{c} C. is taken to be 94074×10^{9}, and this corresponds to a known value of the resistance for a given tube.

The liquid whose resistance was to be measured was placed in a capillary tube which opened out at both ends into wide limbs at right angles to the capillary.

Fig. 2.

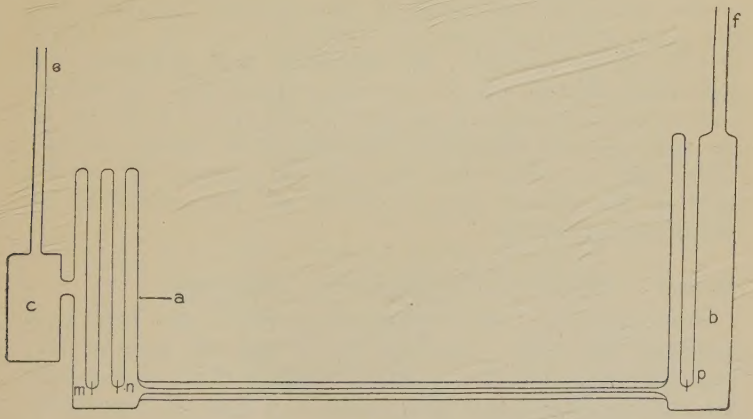


Glass tubes or leads (*a*), fig. 2, into which platinum wires (*b*) were sealed, fitted into the limbs. The leads were held in position by ground-glass joints at (*c*), and

were about half-filled with mercury, into which were placed copper wires (*d*), the length of wire immersed being always the same so that the resistances of the leads were always the same at the same temperature. The copper wires were connected to the bridge by flexible wires, and in order to eliminate any change in the resistance of the wires during an experiment, a pair of flexible compensating wires were also connected to the bridge. The resistances between the platinum points when the leads were, firstly, in the same cup of mercury and, secondly, in the limbs of the capillary tube, were measured in every determination, and the difference between these resistances was taken as the resistance of the mercury in the capillary tube.

For metals which oxidize in amalgams a tube which could be evacuated (fig. 3) was used.

Fig. 3.



The side limbs "a" and "b" were fused on to the capillary, and to "a" was fused another side vessel "c." The tube was open to the air at "e" and "f." Platinum points were sealed on to the leads "m," "n," and "p," which were fixed in the tube. The tube was thoroughly cleaned and dried, mercury placed in "b" and the metal was added at "e," so as to remain in the side vessel "c" separate from the mercury. The tube was connected to a Töpler pump and a bulb containing phosphorus pentoxide and then evacuated to a pressure of ·01 mm., the pressure being measured by means of a McLeod gauge. Dry hydrogen was then allowed to pass into the tube to a

pressure sufficient to give one atmosphere at the highest temperature at which the resistance was to be measured. The tube was then sealed off at "e" and "f," and the mercury allowed to run into the vessel "c" on to the metal. When the metal had completely dissolved, the amalgam was poured back into the capillary and the measurements made. The resistance of the tube, containing pure mercury, was determined at different temperatures, and by comparing the values of the temperature coefficient with the corrected values obtained with the quartz tube, the correction for the expansion of the glass was found.

The resistance of the liquid in the capillary was taken as the difference between the resistances when the leads were firstly in "n" and "p," and secondly in "m" and "n."

Thermoelectric Currents.

When the galvanometer circuit was closed, a deflexion of the mirror was produced by thermoelectric currents, and the point of balance on the bridge could not be found by the usual method. To overcome this difficulty, the galvanometer arm was always kept closed and the bridge was adjusted so that there was no change of deflexion of the galvanometer mirror on completing the battery circuit. When this condition was obtained, the value of the resistance is the correct one in virtue of the properties of conjugate conductors.

Method of Heating and of Measuring Temperature.

For measuring the resistance at 0° C. the tube and mercury cup were immersed in a bath of melting ice, and for measurements at room temperature a water-bath was used. For higher temperatures a bath of vigorously boiling liquid, of an appropriate boiling-point, was used. The following liquids, having the specified boiling-points, were used :—Water (100° C.) ; aniline (184° C.) ; eugenol (256° C.) ; diphenylamine (300° C.).

It was found that the temperatures of the boiling liquids increased with continued heating, until a steady temperature was reached. Observations were not made until this constant temperature was reached ; a series of measurements of temperature, and of the resistance with the leads in the same column of liquid (cup A, fig. 4) and in the tube, were taken to ensure constant results. The resistances were found to be constant to within ·0001 ohm.

The possible error in each of these measurements was less

than ·0001 ohm, so that the possible error in the resistances of the liquid was less than ·0002 ohm.

The temperature was measured by means of a platinum resistance thermometer and a set of mercury thermometers. The platinum thermometer was calibrated in melting ice, steam, and the vapour of boiling mercury, and the constant δ in the equation

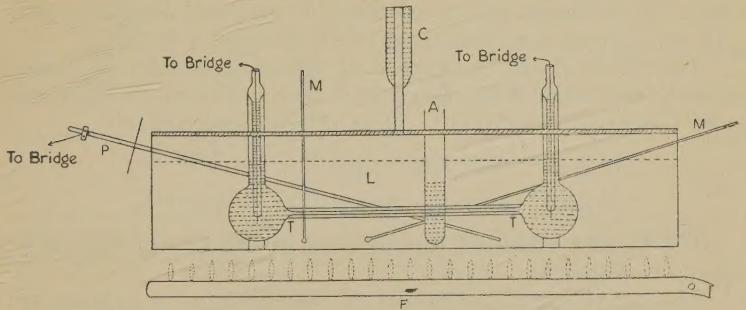
$$t - t_{pt} = \delta \left\{ \left(\frac{t}{100} \right)^2 - \frac{t}{100} \right\}$$

was found to be 1·51.

The mercury thermometers, covering a range 0° C. to 300° C., were calibrated against the platinum thermometer.

Fig. 4 shows the arrangement of the thermometers and tube in the bath.

Fig. 4.



T = Tube containing mercury or amalgam.
A = Cup containing mercury or amalgam.
P = Platinum thermometer.
M = Mercury thermometers.
L = Liquid to be boiled.
C = Reflux condenser.
F = Burner.

The formation of bubbles in the capillary tube, especially at high temperature, was a source of much trouble. To avoid this, the tube and mercury were separately heated to the boiling-point of mercury, and the hot mercury added to the tube. Both were then heated to a temperature above that at which the resistance was to be measured, and the tube was carefully examined for bubbles by means of a lens, and any bubbles left were removed.

After each determination at a high temperature, the resistance of the mercury was measured after it had cooled to room temperature, and if this value was correct it was assumed that no bubbles had formed at the high temperature.

Experimental Results.

E. J. Williams * determined the temperature coefficient of the electrical resistance of mercury between 0° C. and 300° C., using a glass tube, and applied corrections due to the expansion of the glass on heating. These corrections were of the order of 1 per cent., and involved the determination of the average coefficient of linear expansion of the glass envelope over certain ranges of temperature. Owing to the difficulty of measuring the coefficient of expansion accurately, and its comparatively rapid rise with temperature, it was considered advisable to repeat the experiments with mercury under conditions which made the corrections for the expansion of the containing envelope of far less consequence.

For this purpose, the mercury was contained in a tube (fig. 1) of fused quartz of diam. 1 mm. and length about 37 cm., giving a resistance at 0° C. of about 0·5 ohm.

The value of the coefficient of linear expansion of fused quartz was taken from Kaye and Laby's Tables of Physical and Chemical Constants †. The values given are :—

$\cdot 50 \times 10^{-6}$ over the range 0° C. to 100° C.,

and $\cdot 54 \times 10^{-6}$ over the range 0° C. to 1000° C.

The results obtained for mercury in the quartz tube are given in Table I.

The temperature coefficient of resistance of a column of mercury of constant dimensions is the same as the temperature coefficient of the resistivity of mercury. The former is given in column 5, and the resistivities of mercury at various temperatures are given in column 6, the resistivity at 0° C. being assumed to be $94 \cdot 074 \times 10^{-6}$, and the values at the different temperatures being calculated from the corrected values of the average temperature coefficient given in column 5. The conductivity of mercury at the various temperatures is given in the last column. The percentage probable error in the resistivity and conductivity is estimated to be on the average about ·02.

The resistivity over the range of temperatures examined can be represented by the equation

$$\rho = \rho_0(1 + at + bt^2 + ct^3),$$

where ρ_0 is the resistivity at 0° C. and a, b, and c are constants.

* *Loc. cit.*

† Kaye and Laby's 'Tables of Physical and Chemical Constants,' p. 53.

TABLE I.

Temperature in degrees centi-grade.	Resistance in ohms.	Average temperature coefficient of resistance for the range 0° C. to t° C. (uncorrected for expansion of quartz) $\times 10^4$.	Correction due to expansion of quartz $= +\frac{R}{R_0} g \times 10^4$.*	Corrected average temperature coefficient of resistance for the range 0° C. to t° C.	Resistivity at t° C. $\times 10^9$.	Conductivity at t° C. $\times 10^1$.
0	·49500	.....	.....	.....	94074	106300
14·8	·50160	9·009	·005	9·014	95328	104901
100	·54385	9·868	·005	9·873	103361	96749
168·9	·58330	10·561	·006	10·567	110863	90201
255·5	·64080	11·528	·006	11·534	121797	821038
300	·67275	11·970	·007	11·977	127876	78201

* R is the observed resistance of mercury filling the capillary at a temperature t° C. ; R_0 is the resistance at 0° C., and "g" the average coefficient of linear expansion of the glass from 0° C. to t° C.

The values of the constants a, b, and c, which represent with great accuracy the variation of resistivity with temperature, are :

$$a = \cdot 0_3 8877,$$

$$b = \cdot 0_6 977,$$

$$c = \cdot 0_9 19.$$

The variation of resistivity of mercury with temperature is therefore given by the equation :

$$\rho_t = \rho_0 \{1 + \cdot 0_3 8877\, t + \cdot 0_6 977\, t^2 + \cdot 0_9 19\, t^3\},$$

and the values of the resistivity calculated from the formula agree with those determined experimentally within about ·02 per cent. on the average.

It is not proposed here to compare the results obtained in the present experiments with those obtained by other

investigators*, except to point out that the values of the resistivity and conductivity are in good agreement with those obtained by Williams, who found

$$\rho_t = 94074\{1 + \cdot 0_3 8879\, t + \cdot 0_6 975\, t^2 + \cdot 0_9 20\, t_3\}.$$

The Electrical Conductivities of Dilute Thallium Amalgams.

The conductivity of thallium amalgams has been examined by Bornemann and Rauschenplatt †, and by Pavlovitsch ‡, whilst Feninger § considered the electrical conductivity of dilute amalgams in relation to internal friction. Pavlovitsch examined the electrical conductivity of alloys containing from 0 to 40 per cent. of thallium, and the curve obtained shows a maximum for about 27 per cent. of thallium.

Feninger determined the relative conductivity with respect to mercury of thallium amalgams of the following atomic per cent.:—0·156, 0·308, 0·650 at temperatures 0°, 20°, 40°, 60°, 10°, and 18° C.

Bornemann and Rauschenplatt obtained the following results for the resistivity of dilute thallium amalgams:—

Atomic per cent. of Tl.	Specific Resistance $\times 10^4$.					
	50°	100°	150°	200°	250°	300°
0·98	·9658	1·0112	1·0622	1·1179	1·1820	1·2514
2·85	·9320	·9741	1·0210	1·0700	1·1208	1·1820

In the present experiments the specific resistances of thallium amalgams of concentrations varying from 0·063 gram of thallium in 100 grams of mercury, to 1 per cent. of thallium in mercury, were examined at room temperature and 100° C., and an amalgam of concentration 0·5 gram of thallium per 100 grams of mercury at higher temperatures up to about 300° C.

* J. W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' vol. iv. pp. 729–732. Williams, *loc. cit.*

† Bornemann & Rauschenplatt, *Metallurgie*, ix. p. 510 (1912).

‡ Pavlovitsch, *Russ. Phys. Chem. Soc.* xlvii. p. 29 (1915).

§ Feninger, *loc. cit.*

Owing to the rapid oxidation of the amalgams, the experiments were carried out in a vacuum or in an atmosphere of hydrogen (for high temperatures) in the apparatus previously described (fig. 3). The results are collected in Tables II., III., and IV.

In Table II. the concentration "c" is expressed in gram atoms per 100 gram atoms of mercury, *i. e.* in atom atoms per cent. approximately. The tables are self-explanatory.

TABLE II.

Thallium Amalgams.

Temperature $t°$ C.	Percentage weight of thallium in mercury.	Concentration "c."	Resistivity of pure mercury at $t°$ C. $\times 10^9$.	Conductivity of mercury at $t°$ C. $\times 10^1$.	Resistivity of amalgam $\times 10^9$.	Conductivity of amalgam at $t°$ C. $\times 10^1$.
13·3°	·0634	·0622	95200	105042	95083	105172
	·1275	·1252	,,	,,	94963	105305
	·2250	·2505	,,	,,	94727	105566
	·3826	·3758	,,	,,	94492	105829
	·5003	·4914	,,	,,	94278	106070
	·7494	·7361	,,	,,	93820	106587
	1·0000	·9823	,,	,,	93375	107095
100°	·0634	·0622	103361	96749	103216	96884
	·1275	·1252	,,	,,	103076	97016
	·2550	·2505	,,	,,	102800	97276
	·3826	·3758	,,	,,	102517	97544
	·5003	·4914	,,	,,	102249	97800
	·7494	·7361	,,	,,	101698	98330
	1·0000	·9823	,,	,,	101159	98854
13·3°	·5003	·4914	95200	105042	94278	106070
100	,,	,,	103361	96749	102249	97800
183	,,	,,	112544	88854	110910	90163
255·5	,,	,,	121797	82104	119788	83481
294·8	,,	,,	127137	78654	124448	80355

Bornemann and Rauschenplatt's results show that the temperature coefficient of resistivity of the amalgams decreases with increase of temperature. This is contrary to the results found in the present experiments. The resistivity of an amalgam of concentration "c" = ·98 at 100° found in these experiments is very close to the value given by Bornemann and Rauschenplatt, the values differing by only ·04 per cent.

Curve I.

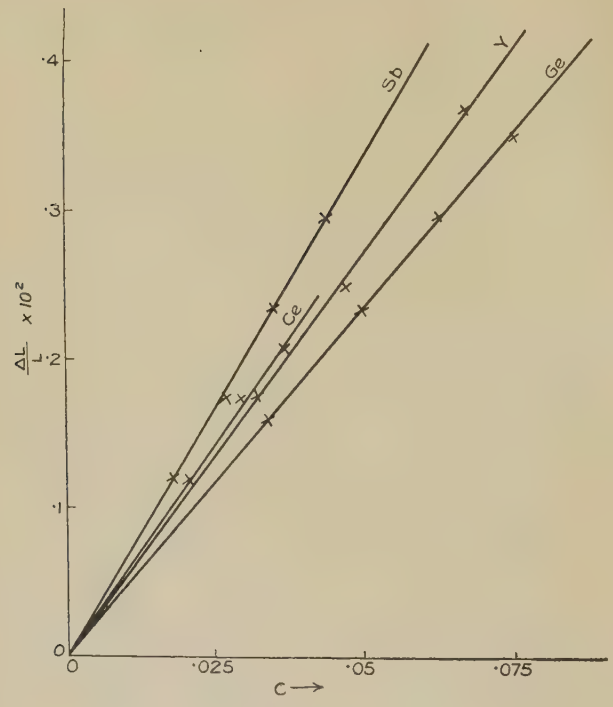


TABLE III.

Variation of the resistivity of an amalgam of Thallium of concentration "c" = ·4914 with temperature.

Temperature $t°$ C.	Resistivity of amalgam at $t°$ C.	Average temperature coefficient of resistivity $13·3 - t°$ C. for mercury $\times 10^4$.	Average temperature coefficient of resistivity $13·3 - t°$ C. for amalgam $\times 10^4$.	$\frac{\Delta L}{L} \times 10^2$.
13·3°	94278	.....	.....	·978
100	102249	9·888	9·752	1·0866
183	110910	10·736	16·396	1·4731
255·5	119788	11·535	11·172	1·6774
294·8	124448	11·917	11·368	2·1633

In Table III. $\frac{\Delta L}{L}$ is the increase of conductivity relative to that of mercury at the same temperature. For the same concentration it increases with temperature.

Table IV. shows the average temperature coefficient of the various amalgams of different concentrations between 13°·3 C. and 100° C. The average temperature coefficient diminishes as the concentration increases.

TABLE IV.

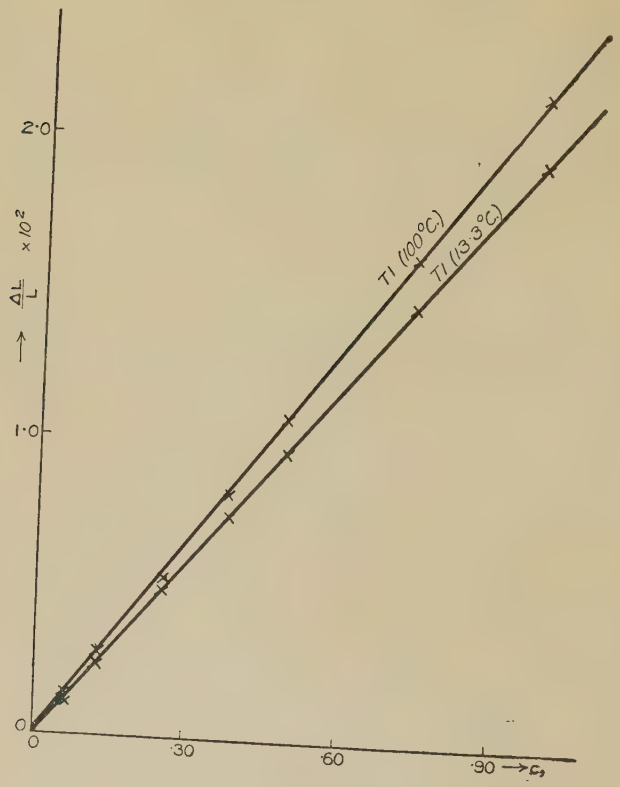
Average temperature coefficient of resistivity of Thallium Amalgam between 13°·3 and 100° C.

Concentration "*c*."	Temperature coefficient of resistivity of amalgam between 13°·3 and 100° C. $\times 10^4$.
·0622	9·866
·1252	9·854
·2505	9·829
·3758	9·796
·4914	9·752
·7361	9·685
·9823	9·615

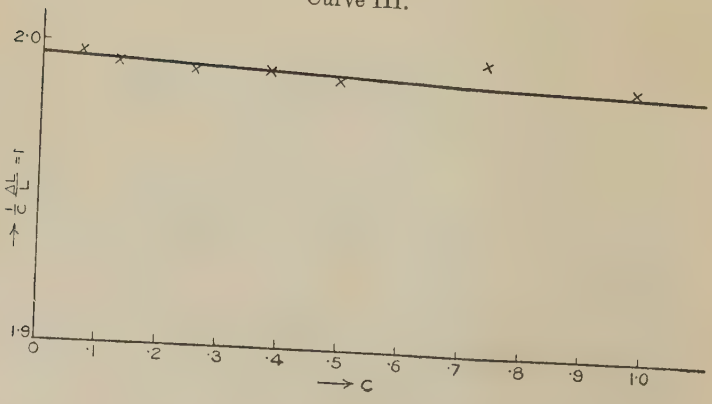
Curve II shows the variation of the relative increase of conductivity $\frac{\Delta L}{L}$ with concentration "*c*" at 13°·3. Since it is a straight line, the increase of conductivity relative to mercury is proportional to the concentration for dilute amalgams of thallium. Curve II also gives the variation of $\frac{\Delta L}{L}$ with "*c*" at 100°.

This again is a straight line, showing that $\frac{\Delta L}{L}$ is proportional to "*c*" at 100° C.

Curve II.



Curve III.



Curve III gives the variation of $\frac{1}{c}\frac{\Delta L}{L}$ with "c" at 13°·3, *i. e.*, the variation of the ratio of the increase of conductivity relative to mercury, to the concentration, with the concentration. It is practically a straight line for dilute solutions.

From this curve, the value of l_∞, the ratio of the relative increase of conductivity with respect to mercury to the concentration, at infinite dilution, is obtained.

The Electrical Conductivity of Germanium Amalgams.

As far as the author is aware, no previous determination of the conductivity of germanium amalgams has been made, and the measurements are rather difficult, on account of the low solubility of germanium in mercury. It was found necessary to heat the mercury to a temperature of about 250° C. before any appreciable quantity of germanium would pass into solution, and all measurements, with one exception, were carried out at temperatures of about 300° C. The determinations of the resistance of the amalgams were made as in the previous experiments, the quartz tube being used. The amalgams were heated for several hours in the bath at about 300° C. in order to ensure that the metal had diffused through the capillary, and until a constant value of the resistance was obtained.

The mercury in the cup was replaced by a germanium amalgam of the same concentration as that in the capillary tube, so that the leads were always in the same amalgam during the two measurements taken to obtain a value of the resistance. This precaution was taken in all experiments carried out on amalgams. The results are given in Tables V. and VI.

Curve I shows the variation of the relative increase of conductivity, with respect to mercury, with concentration. It is seen that these quantities vary proportionately.

From the results obtained at 250°·1 C. it is seen that the average temperature coefficient of resistivity of the amalgam is slightly less than that of mercury.

Since the amalgams are so extremely dilute, the value of l_∞, the ratio of the increase of conductivity relative to mercury to the concentration, at infinite dilution, is taken as the mean of the values of $\frac{1}{c}\frac{\Delta L}{L}$ obtained. The values of this quantity for dilute amalgams are not very accurate owing to the small changes in conductivity produced, and errors of from 4 to 10 per cent. are possible on the average.

TABLE V.

Nature of Amalgam.	Temperature $t°$ C.	Percentage weight of substance in mercury.	Concentration "c."	Resistivity of mercury at $t°$ C. $\times 10^9$.	Conductivity of mercury at $t°$ C. $\times 10^1$.	Resistivity of amalgam at $t°$ C. $\times 10^9$.	Conductivity of amalgam at $t°$ C. $\times 10^1$.
Germanium	301·8°	·01227	·03392	128140	78040	127933	78166
	,,	·01824	·05042	,,	,,	127838	78224
	,,	·02283	·06310	,,	,,	127762	78271
	,,	·02724	·07529	,,	,,	127691	78314
	250·1°	·01824	·05042	120988	82652	120729	82830
Antimony	301·8°	·01096	·01827	128140	78040	127984	78135
	,,	·01617	·02696	,,	,,	127915	78177
	,,	·02107	·03513	,,	,,	127838	78224
	,,	·02650	·04418	,,	,,	127761	78271
Yttrium	302°	·01450	·03272	128169	78022	127943	78160
	,,	·02120	·04784	,,	,,	127849	78217
	,,	·03000	·06770	,,	,,	127701	78308
	,,	·04220	·09523	,,	,,	127494	78435
Cerium	300°	·01440	·02058	127876	78201	127720	78296
	,,	·02090	·02986	,,	,,	127655	78336
	,,	·02500	·03572	,,	,,	127611	78363
Aluminium	300°	·01000	·07395	127876	78201	127405	78490
	,,	·01953	·14442	,,	,,	126992	78745

TABLE VI.

Nature of Amalgam.	Temperature $t°$ C.	Concentration "c."	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{c}\frac{\Delta L}{L} \times 10^2$.	$l_\infty \times 10^2$.
Thallium	13·3°	·06220	·1243	1·997	1·995
	,,	·1252	·2497	1·994	
	,,	·2505	·4991	1·992	
	,,	·3758	·7488	1·993	
	,,	·4914	·9780	1·990	
	,,	·7361	1·4710	1·998	
	,,	·9823	1·9543	1·990	
	100°	·0622	·1394	2·241	2·208
	,,	·1252	·2760	2·205	
	,,	·2505	·5450	2·176	
	,,	·3758	·8220	2·187	
	,,	·4914	1·0866	2·211	
	,,	·7361	1·6340	2·220	
	,,	·9823	2·1761	2·215	
	13·3°	·4914	·9780	1·990	
	100·0	,,	1·0866	2·211	
	183·0	,,	1·4731	2·998	
	255·5	,,	1·6774	3·414	
	294·8	,,	2·1633	4·402	
Germanium ...	301·8°	·03392	·1618	4·770	4·7
	,,	·05042	·2359	4·679	
	,,	·06310	·2964	4·697	
	,,	·07529	·3505	4·655	
	250·1°	·05042	·2155	4·274	
Antimony	301·8°	·01827	·1213	6·639	6·6
	,,	·02696	·1751	6·495	
	,,	·03513	·2359	6·715	
	,,	·04418	·2966	6·713	
Yttrium	302·0°	·03272	·1765	5·394	5·4
	,,	·04784	·2501	5·228	
	,,	·06770	·3668	5·418	
	,,	·09523	·5291	5·556	
Cerium	300·0°	·02058	·1210	5·88	5·8
	,,	·02986	·1730	5·79	
	,,	·03572	·2070	5·79	
Aluminium ...	300·0°	·07395	·3702	5·01	5·0
	,,	·14442	·6952	4·81	

The Electrical Conductivity of Antimony Amalgams.

The experiments on antimony amalgams were carried out in the quartz tube, as the metal amalgam does not oxidize appreciably. Owing to the low solubility of antimony in

mercury, only very dilute amalgams of concentration ·018 to ·044 were used and their resistances found at about 300°, as the mercury had to be heated up to about this temperature before the metal would dissolve.

The results for the four amalgams are given in Tables V. and VI. The relation between $\frac{\Delta L}{L}$ and "c" at 301°·8 is shown graphically in Curve I. It was found that the relative increase of conductivity with respect to mercury is proportional to the concentration "c."

As in the case for all other amalgams, the mercury was heated at about 300° C. for several hours in order to obtain reliable values of the resistances. The value of l_∞ is taken as the mean of the value of $\frac{1}{c}\frac{\Delta L}{L}$, since the amalgams approach infinite dilution.

Yttrium Amalgams.

The electrical resistances of the four yttrium amalgams were found at 302°, using the quartz tube. The same precautions as with the previous amalgams were taken. The amalgams were of concentrations ranging from ·03 to ·09.

The results are shown in Tables V. and VI., and graphically in Curve I.

Since the curve is a straight line, the increase of conductivity relative to mercury is proportional to the concentration.

The value of the ratio of the increase of conductivity relative to mercury, to the concentration for infinite dilution is taken as the mean of the values of $\frac{1}{c}\frac{\Delta L}{L}$, since the amalgams are so dilute.

Cerium Amalgams.

Owing to the oxidation of cerium, when in amalgam, the experiments were carried out in the tube previously described (fig. 3).

The tube was evacuated and filled with pure dry hydrogen to a pressure which increased to one atmosphere at the temperature at which the determinations of resistance were made. Since the solubility of cerium in mercury is very low, three amalgams of concentration between ·02 and ·04 were used at 300°.

Tables V. and VI. show the results obtained, and Curve I gives the variation of $\frac{\Delta L}{L}$ with "c."

The value of $\frac{1}{c}\frac{\Delta L}{L}$ at infinite dilution is taken as the mean of the values obtained for the respective concentrations, as the amalgams were extremely dilute.

Aluminium Amalgams.

A few preliminary experiments were carried out on the conductivity of dilute aluminium amalgams.

Owing to the rapid oxidation of the amalgam in air, the experiments were carried out in an atmosphere of hydrogen. Two amalgams of concentrations 0·0739 and 0·1444 were employed, and the results are given in Tables V. and VI.

The relative increase of conductivity with respect to mercury is approximately proportional to the concentration.

Beryllium Amalgams.

L. F. Nilson and O. Petterson * prepared a beryllium amalgam by the electrolysis of a concentrated solution of beryllium chloride with a mercury cathode. According to W. Ramsay †, the amalgam so prepared is very dilute, since more concentrated amalgams are readily attacked by the electrolyte, and it is readily oxidized in air. An attempt was made to prepare a dilute beryllium amalgam in an atmosphere of hydrogen, and measure its conductivity at about 300° C. About 0·004 gram of beryllium was added to 200 grams of mercury in the sealed apparatus containing hydrogen described previously. The apparatus was kept at a temperature of about 300° C. for several hours, but no change of resistance due to solution of the beryllium in the mercury could be detected. As a change of resistance of one part in eight thousand could be detected by means of the apparatus employed, it was concluded that either beryllium did not enter into solution even at 300° C., or that the amalgam produced was so dilute that its effect on the conductivity was negligible.

Discussion of Results.

For purposes of discussion the Table VI. has been constructed for the results obtained for all the amalgams. The concentration "c" is expressed in gram atoms of the metal per 100 gram atoms of mercury, *i. e.*, approximately in atom atoms per cent.

* *Ber.* xi. p. 381 (1878).
† Journ. Chem. Soc. lv. p. 530 (1889).

$\frac{\Delta L}{L}$ is the increase in conductivity relative to that of mercury at the same temperature.

The fifth column gives the ratio of $\frac{\Delta L}{L}$ to "c," i.e., the values of "l."

The sixth column gives the value of "l" for infinite dilution, *i. e.*, the value of the ratio of the increase of conductivity relative to mercury at the same temperature to the concentration, when the latter is very small.

According to Skaupy's theory, which was discussed in the introduction to this paper, the value of $H_\infty = l_\infty + r_\infty$ should be of the same order of magnitude for the different metals dissolved in mercury. Unfortunately, the author has not at his disposal values of r_∞ for the different amalgams, whose conductivities have been measured, and is consequently obliged to consider the values of l_∞ in relation to the different amalgams. From the values given in Table VI. the conclusion can be drawn that the value of l_∞ is of the same order of magnitude for all the amalgams examined. The values for germanium, yttrium, cerium, and antimony vary from $4{\cdot}7 \times 10^{-2}$ to $6{\cdot}6 \times 10^{-2}$ but the value for thallium is decidedly low, $1{\cdot}995 \times 10^{-2}$ when taken at a temperature of about 13°·3 C.

It is of interest, however, to point out that the value of $\frac{1}{c}\frac{\Delta L}{L}$ for thallium amalgams increases rapidly with temperature, its value changing from $1{\cdot}995 \times 10^{-2}$ at 13°·3 C. to $4{\cdot}40 \times 10^{-2}$ at 294° 8 C. If the latter value is taken for l_∞, it compares reasonably well with the values obtained for the other amalgams at practically the same temperature.

In the present investigation the conductivity of dilute amalgams of the various metals was examined, and there is very little change in the value of "l" with change of concentration. Consequently, there is not much point in discussing the values of $\frac{l_\infty - l}{c}$.

Summary.

1. The resistivity and conductivity of mercury have been measured in a quartz tube at temperatures varying from 0° to 300° C. The specific resistance at any temperature "t" within this range is given by the formula :

$$\rho_t = \rho_0(1 + {\cdot}0_3\,8877t + {\cdot}0_6\,977t^2 + {\cdot}0_9\,19t^3).$$

2. The resistivity and conductivity of dilute amalgams

of thallium, germanium, antimony, yttrium, cerium, and aluminium have been measured. The conductivities of germanium, antimony, yttrium, and cerium amalgams were measured at about 300° C., and the conductivities of amalgams of thallium of various concentrations were determined at 13°·3 C. and 100° C. In the case of thallium amalgams of concentration ·49, the measurements were extended to 300° C. It was found impossible to prepare an amalgam of beryllium of sufficient strength to measure its conductivity.

3. It was found that the relative change of conductivity with respect to mercury at the same temperature is proportional to the concentration for the dilute amalgams employed in these experiments, and that the temperature coefficient of increase of resistance in the case of thallium amalgams decreases with increase of concentration.

4. The results were examined in relation to a theory put forward by Skaupy, and it was found that the value of l_∞, *i. e.*, the value of $\frac{1}{c}\frac{\Delta L}{L}$ at infinite dilution, was of the *same order of magnitude* for the amalgams examined. The meaning of this result is that atom for atom the effect of the different metals on the conductivity of mercury is about the same.

The experiments described above were carried out in the Physical Laboratories of the University College of Swansea. In conclusion, I wish to thank Professor E. J. Evans for his valuable suggestions and guidance during the course of the research.

December 1925.

II. *The Magnetic Susceptibilities of some Alkalis.* By W. Sucksmith, *B.Sc., Lecturer in Physics, University of Bristol* *.

THE experiments described in the present paper are an account of measurements on the susceptibilities of the alkalis over a range of temperatures in the solid and liquid states. The original intention was to try to extend these also to the gaseous state. It has been shown that sodium and potassium † are monatomic in the gaseous state, and for this

* Communicated by the Author.

† Dewar & Scott, Proc. Roy. Soc. A, xxix. p. 490.

reason a knowledge of their susceptibility is desirable as a basis to modern magneton theory. Unfortunately, the difficulty of finding a suitable container above 500° C. proved prohibitive. However, the results obtained in the solid and liquid states are not without interest, and the following is an account of measurements made up to the neighbourhood of 500° C.

The method employed is essentially that of Faraday, in which the force exerted on a small quantity of the substance in a non-uniform magnetic field is measured. The force on an element of mass dm in the direction x is

$$dF = \chi dm H \frac{\partial H}{\partial x},$$

where X is the susceptibility per unit mass, H the magnetic field whose gradient in the direction of the force, *i.e.*, perpendicular to H, is $\frac{\partial H}{\partial x}$. If the volume is limited to one in which the variation of $H\frac{\partial H}{\partial x}$ over the volume occupied by the total mass m is negligible, we can write

$$F = \chi m H \frac{\partial H}{\partial x}.$$

The point at which the substance is placed is that at which $H\frac{\partial H}{\partial x}$ is a maximum, and consequently the error due to accidental displacement is a minimum.

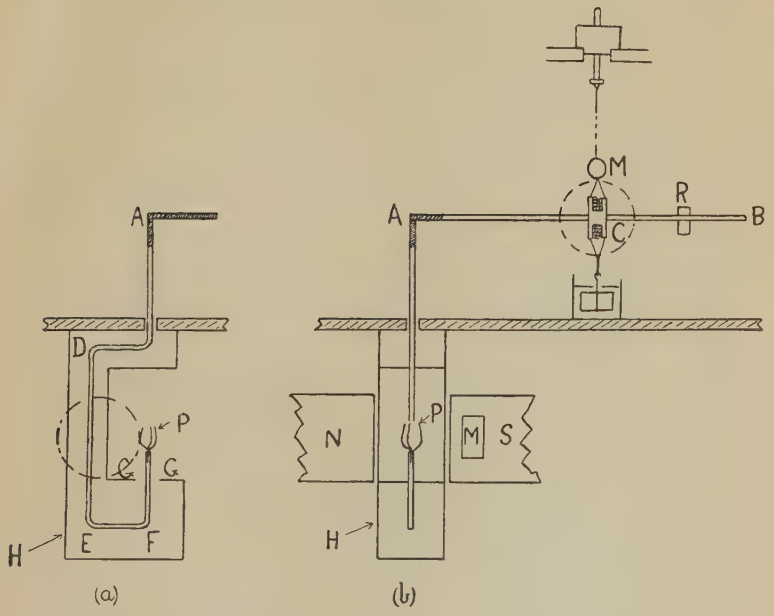
As a non-uniform field is difficult to measure with accuracy, a comparison method was used, the standard adopted being water, whose susceptibility is known accurately.

The force F is neutralized electro-magnetically, and the substance brought back to its original position. In this way, all measurements are made in the position of maximum sensitivity and least error.

The general disposition of the apparatus is shown in fig. 1, (*a*) looking along the direction of, and (*b*) perpendicular, to the direction of the magnetic field. The torsion arm ACB is of thin-walled glass-tubing, supported at C by a suspension of phosphor-bronze strip. The upper end of the strip is attached to a torsion head which carries a three-dimensional adjustment. The length of the suspension is about 7 cm., as it was found that, other things being equal, a short suspension was less affected by extraneous disturbances than

a larger one. An L-shaped piece of copper rod is fixed into A, by means of which the arm ADEF carrying the specimen is attached. This suspension rod is also of thin glass tubing, external diameter 2·5 mm., and carries a platinum fork which holds the phial containing the alkali. The point F is vertically under A, so that no sideways displacement of the system is possible when the phial is placed in the fork.

Fig. 1.



The rider R is used to preserve balance of the torsion arm when different masses are used. To prevent disturbances due to convection currents, a brass box can be placed over the apparatus, whilst on the under side of the table, the arm ADEF is enclosed in the brass case H. The furnace is placed in the position GG.

The inner wall of the furnace consists of a copper tube, closed at one end with a copper plate. This ensures equilibrium of temperature over the specimen. On this copper tube is wound the heating coil of constantan, insulated from it by means of asbestos paper and embedded in a cement composed of water glass and china clay. The whole is

enclosed in a double-walled brass case, so as to allow water cooling. It was found further, that about an inch of water in the brass case H below EF greatly improved the steadiness of the zero at higher temperatures.

The temperature of the furnace was measured by a platinum to platinum-rhodium thermocouple attached to its inner wall, the junction being as close as possible to the position occupied by the phial.

At C is the neutralizing coil which is situated midway between two fixed Helmholtz coils (indicated by a dotted circle in fig. 1 *b*), the turns being at right angles to those of the moving coil. The current is passed through the coil by means of long spiral leads of 48 S.W.G. copper. These leads are not sufficient to affect the torsion constant appreciably, and, furthermore, any such effect merely alters the sensitivity slightly. To the lower end of the coil C is fixed a damping vane immersed in a mixture of lubricating oil and paraffin of such consistency as to make the system dead-beat.

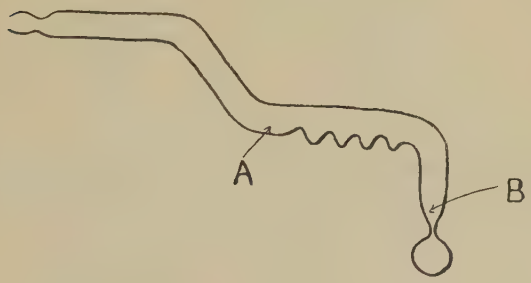
The Helmholtz coils and the moving coil are in series with a mirror dynamometer of low impedance, through which alternating current can be passed to neutralize the displacement due to the magnetic forces. The deflexion of the dynamometer is noted and the mean direct current producing the same deflexion is measured on a standard milliammeter. The square of this current is proportional to the magnetic force on the phial and its contents.

Alternating current is necessary owing to the large stray field of the electromagnet in which the coil C moves. The source of this A.C. was a motor alternator run off a direct current battery. This is essential in order to keep the voltage quite steady. The frequency was about 40 cycles, whilst that of the A.C. used for heating the furnace was 93, so that no interaction can occur. The current is cut down to a suitable value by non-inductive resistances, which are sufficient to swamp the inductive lag in the dynamometer and coils.

The substances dealt with must as far as possible be free from ferromagnetic impurity. Further, special precautions must be taken to prevent oxidation of the metal before it is sealed into its container. Various materials were tried for use as container, and, finally, "Pyrex" glass was found most suitable. The alkalis, even Cs, have little action on this material over the range of temperature employed, and the evacuated thin-walled phials used only begin to soften at about 550° C.

The metal was originally contained in evacuated glass tubes, which were broken under water-free naphtha. About 1 gm. of the substance was cut off and quickly dried on filter paper and introduced into a "Pyrex" tube of the shape shown in fig. 2. (The diameter of the tube and phial was about 1·2 cm.) This was immediately connected with pressure tubing to an evacuated reservoir and high vacuum pump, which reduced the pressure immediately to 1 or 2 cm. The pump lowered this to 0·1 mm. in a few minutes, so that oxidation was kept small. As soon as the minimum pressure was reached, the metal at A (fig. 2) was gently heated until

Fig. 2.



melted, and kept at 200° to 300° C. for about half an hour until the absorbed gas was released and pumped off. During this procedure, the small quantity of naphtha which had adhered to the metal was deposited on the walls of the tube as a black scale, or left behind on the corrugations of the tube when it was tilted to run the metal into space B above the phial. Successive heating and cooling resulted in drawing the required quantity into the phial. After a final heating, the phial was sealed and melted off at the constriction, the resulting projection being heated to redness and then depressed with a carbon rod, so as to make the phial as near spherical as possible.

The electromagnet used was of the Du Bois type. In order to obtain a large enough space for the introduction of the furnace, the pole pieces, 8 cm. diameter, were fixed at about 5 cm. apart. The faces of the pole pieces, NS in fig. 1*b*, are inclined at 10° to each other, so that the position at which $H\frac{\partial H}{\partial x}$ is a maximum is about 5 cm. outside the line joining their centres. The centre of the phial was placed at

this point in all determinations, adjustments being made by means of a travelling microscope. The position midway between the two pole faces was adjusted by viewing the phial directly, and the position perpendicular to the lines of force by means of reflexion at a plane mirror M attached to the pole piece S inclined at about 45° to the line of sight.

Let ι_1 be the mean neutralization current for the substance and phial,

ι be that for the phial alone,

ι_2 be that for the phial and water occupying the same volume as the substance originally occupied, and χ_a, χ_w and χ the specific susceptibilities of air, water, and substance, respectively. If the phial be placed in the same position for each determination, then

$$\mathrm{K}(\iota_1^2-\iota^2) = (\chi \mathrm{M} - \chi_a m_a)\mathrm{H}\frac{\partial \mathrm{H}}{\partial x},$$

$$\mathrm{K}(\iota_2^2-\iota^2) = (\chi_w m_w - \chi_a m_b)\mathrm{H}\frac{\partial \mathrm{H}}{\partial x}.$$

In these equations K is a numerical constant, m_a the mass of air occupying the internal volume of the phial, M the mass of substance in the phial, and m_b the mass of air occupying the same volume as the water. From this it is seen that

$$\chi = \frac{1}{\mathrm{M}}\left\{\chi_a m_a + (\chi_w m_w - \chi_a m_b)\frac{\iota_1^2-\iota^2}{\iota_2^2-\iota^2}\right\}.$$

The specific susceptibilities of water and air are taken as $-0{\cdot}72\times10^{-6}$ and $+23{\cdot}8\times10^{-6}$, respectively, at 20° C.

At ordinary temperatures measurements were taken at fields corresponding to 4, 6, 8, 10, and 12 amperes, whilst with varying temperatures the field used was that due to 10 amperes. The constancy of susceptibility with different fields shows the absence of ferromagnetic impurity. The Na and K contained no detectable trace of iron. In the case of Rb and Cs, slight quantities were present, presumably due to the method of preparation, which is usually that of electrolysis using an iron electrode. The lithium used (Kahlbaum) contained so much iron as to make measurements impossible. In the case of Cs and Rb measurements at different fields were taken at various temperatures throughout the range in order to eliminate the effect of ferromagnetic impurity by the method due to Owen *. This takes advantage of the fact that for high values of the magnetizing

* Owen, *Ann. der Phys.* xxxvii. p. 657 (1912).

field, whilst the susceptibility of para- and dia-magnetic substances is independent of the field, that of ferromagnetic substances varies inversely as the field.

In taking measurements at different temperatures, the intervals in the neighbourhood were about 5° C. around the melting-point and 20°–50° over the liquid state. Sufficient time was allowed to elapse between measurements to allow the substance and phial to come to temperature equilibrium.

After a series of measurements had been made, the substance had to be removed from the phial to allow the susceptibility of the latter to be measured over the same range. To do this, two narrow cuts were filed through the neck of the phial, after which it was placed in methylated spirit (containing 5 to 10 per cent. water) to remove the alkali. This method was successful for Na and K, but far too vigorous for removing Cs and Rb, owing to their great affinity for water. For these substances, the phial was cut as before and placed in an evacuated tube. The majority of the metal was distilled off, and the small residue removed with alcohol. The amount of glass filed off was less than 1 per cent. of the total weight of the phial, which has a small diamagnetic susceptibility, so that the error involved is negligible.

The results for Na, K, Rb, and Cs are shown in fig. 3, the curves representing the means of 6, 4, 2, and 2 results respectively, the mass susceptibility decreasing with increasing atomic number. Honda * and Owen † have experimented on these substances and found that their susceptibilities remain constant over a range of temperature from −170° to +10° C. There is no satisfactory theory explaining the fact that a large number of elements exhibit a paramagnetic susceptibility independent of temperature. It seems probable that with these elements the decrease with increasing atomic number is due to the increasing diamagnetic contribution of the L, M, and N rings, on which is superposed a paramagnetic effect presumably due to the additional electron.

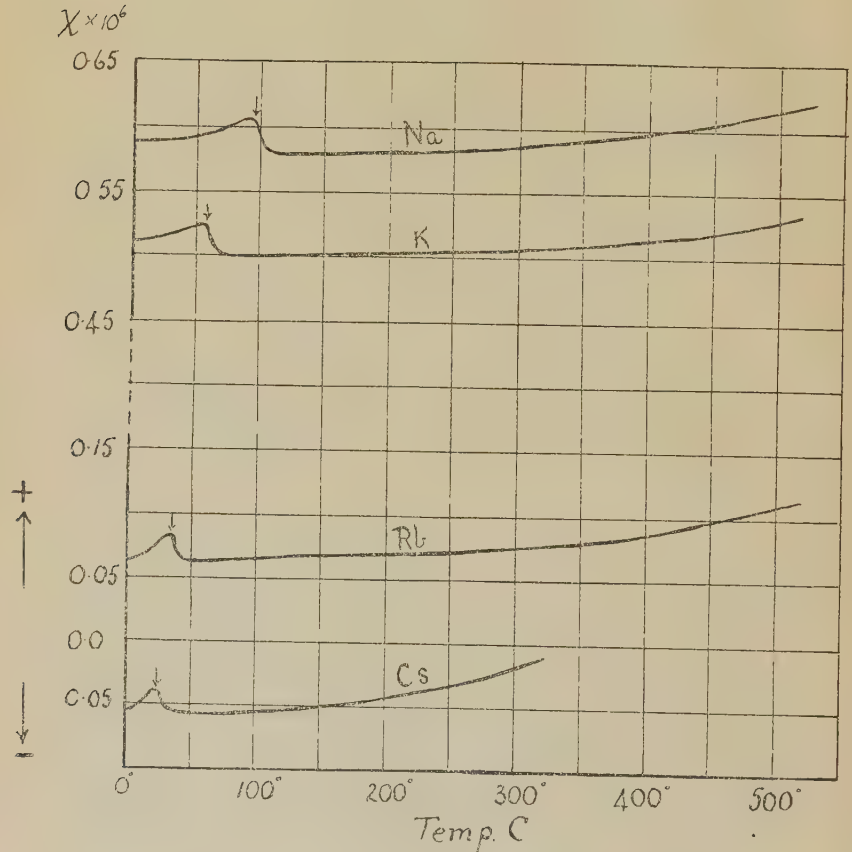
There is gradual change in susceptibility up to the melting-point for each of the substances, followed by a sudden change when fusion takes place. These changes may be explained in the light of the following evidence.

Oxley ‡ has shown that the usual order of change of susceptibility (about 5 per cent.) on crystallization demands

* Honda, *Ann. d. Phys.* xxxii. p. 1027 (1910).
† Owen, *loc. cit.*
‡ Oxley, Phil. Trans. Roy. Soc. A, ccxiv. p. 109 (1914).

the existence of a local molecular field of 10^7 gauss. This leads to an estimate of the potential energy, associated with the crystalline state as a result of the molecular grouping equal to $\frac{1}{2}H_cI$ ergs per unit volume, where H_c is the molecular

Fig. 3.



field, and I the local intensity of magnetization per unit volume. The thermal equivalent of this will in general represent the latent heat of fusion, but a small fraction of the energy may be dissipated before fusion is reached. This would add to the normal variation of specific heat with temperature an additional positive term. It appears that

this is actually the case with sodium. Griffiths * has shown that this metal shows an abnormal rise of specific heat up to the melting-point, followed by a subsequent decrease after fusion has taken place. Further evidence to support this view lies in the fact that sodium † and potassium ‡ both give well-defined X-ray diffraction patterns at the temperature of liquid air, whilst at ordinary temperatures they give no effect. Increase of temperature has evidently broken up the crystal lattice before fusion takes place. These facts seem to support the view that the shape of the susceptibility curves around the melting-point is due to the breaking up of molecular aggregates.

The gradual increase after fusion leads one to look for the cause as being due to the presence of alkali vapour in the space above the liquid. This was negatived by measurements on a phial of 2 c.c. capacity containing about one-tenth that volume of sodium, whereas the vacuous space was usually about 0·3 c.c. in a phial of 1·5 c.c. capacity.

The specific susceptibilities are $+0{\cdot}62$, $+0{\cdot}53$, $+0{\cdot}11 \times 10^{-6}$ for Na, K, and Rb respectively at 500° C. and $-0{\cdot}02 \times 10^{-6}$ at 300°. for Cs. It is interesting to compare these values with those which would be given by allotting one Bohr magneton to each of these substances in the vapour state. At the boiling-points these would be 14·2, 9·2, 4·2, and $3{\cdot}0 \times 10^{-6}$ respectively. If this is to hold, very great increases of susceptibility in the range between 500° C. and the boiling-points must take place.

In conclusion, the writer wishes to express his indebtedness to the Colston Research Society of the University of Bristol for a grant towards expenses, and to Prof. A. M. Tyndall for his interest during the progress of the work.

* E. Griffiths, Proc. Roy. Soc. A, lxxxix. p. 561 (1914).
† Hull, Phys. Rev. (2) x. p. 661 (1917).
‡ McKeehan, Proc. Nat. Acad. Sci. viii. p. 254 (1922).

III. *Determination of the Size and Weight of Single Submicroscopic Spheres of the Order of Magnitude* $r = 4.10^{-5}$ *cm. to* 5.10^{-6} *cm., as well as the Production of Real Images of Submicroscopic Particles by means of Ultraviolet Light.* *By* FELIX EHRENHAFT, *Dr.Phil., Acting Professor of Physics and Head of Physics Institute III. of the University of Vienna, and* EMANUEL WASSER, *Dr.Phil., of Vienna* *.

[Plate I.]

§ 1. *Introduction.*

AS is well known, it is possible to hold single electrically charged colloidal test bodies between the plates of a horizontal condenser, to illuminate the space between the plates with a microscope objective, and to make observations with a microscope adjusted perpendicular to the direction of illumination against a dark background. This procedure was devised by Ehrenhaft †, and has recently been described anew in the Philosophical Magazine ‡. The smaller the diameter of the condenser plates (9 mm. to 2 mm.), the greater may be the aperture of the microscope objective applied in this procedure.

§ 2. *Method of Weight Determination.*

The problem of the determination of the magnitude of submicroscopic bodies appears to have become of great importance for many problems of modern physics. The methods of the determination of magnitude can be free from objection only under the condition that they be carried out independently of other important physical effects of the same order of magnitude §. They must, for example, be independent of the assumption of the existence or non-existence of an elementary quantum of electricity, as well as of the question as to divisibility or indivisibility and equality of charge on the various test bodies. In this way

* Communicated by the Authors.

† F. Ehrenhaft, *Anz. d. Wien. Akad. d. Wiss.* no. vii. March 4, 1909; no. x. April 21, 1910; no. xiii. May 12, 1910.

‡ F. Ehrenhaft, Phil. Mag. vol. xlix. April 1925, p. 633.

§ F. Ehrenhaft, *Phys. Zeits.* xii. p. 102 (1911); Discussion at the "Deutscher Naturforschertag in Jena," R. Bär, *Phys. Zeits.* xxii. p. 617 (1921).

there arose the idea * of determining in a purely mechanical way a law of resistance for small spheres moving in a gas by means of velocity measurements carried out on the same test bodies at different gas pressures. Up to the present time this was successful only for test bodies of magnitudes down to $3{\cdot}5 \cdot 10^{-5}$ cm. The critical and interesting colloidal order of magnitudes begins just at this point.

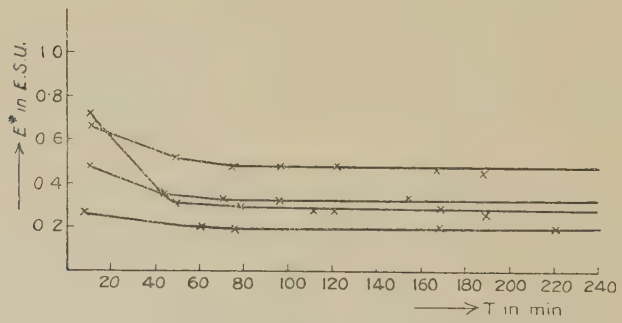
Two circumstances have prevented the setting up empirically of a law of resistance for this order of magnitude. First may be mentioned the difficulty in the selection of a suitable material for experiment. A fluid would appear to come at first into consideration. All fluids however, with the exception of mercury, are exceptionally transparent, so that it would be difficult to render them visible against a dark background when in this state of fine division. In the second place, fluids evaporate. Further, the uniform velocity of fall of these fluid droplets in a resisting medium (gas) is, on account of their small density, so small that the experiments would seem to have little hope of success, for the vertical component of the Brownian movement would in this case be a disturbing factor. We are hence limited for the first to mercury. The mercury droplets produced by evaporation, pulverization, etc. have a very great reflecting power and a sufficiently great velocity of fall. The second

* It was M. Reinganum who first pointed out that it would be possible to reach a decision concerning the law of resistance by making observations on the same test body at different pressures (M. Reinganum, *Verh. d. Deutsch. phys. Ges.* xii. p. 1025, 1910). E. Meyer and W. Gerlach then observed the same test body at different gas pressures in a condenser of the same dimensions as Millikan's (E. Meyer and W. Gerlach, *Ann. d. Phys.* xlvii. p. 244, 1915). Following this, I. Parankiewicz observed the same selenium sphere at several pressures in an Ehrenhaft condenser and demonstrated the validity in these test bodies of Cunningham's correction to Stokes's law (I. Parankiewicz, *Phys. Zeits.* xix. p. 280, 1918). In the discussion at the Physikertag in Jena about the hypothesis of small densities (Bär), F. Ehrenhaft referred anew to the experimental determination of the law of resistance, demanded by him in 1911, and suggested gold in inert gases as suitable material for experiment (*loc. cit.*). Th. Sexl recently computed the Cunningham correction factor from the observations of Millikan and Derieux on a non-evaporating mercury drop and found it to be 0·86 (Th. Sexl, *Z. f. Phys.* xxvi. p. 371, 1924). Finally J. Mattauch, experimenting in our institute with sprayed oil, proved in a purely mechanical way the validity of the law of resistance, which agrees with that of Millikan. He did it by varying the pressure around differently sized oil-drops of microscopic order of magnitude and did not make use of the assumption, used by Millikan, of the equality of the charges on different drops (existence of an elementary quantum) (J. Mattauch, *Z. f. Phys.* xxxii. p. 439, 1925).

condition, the constancy of mass, has however not yet been clarified for these test bodies.

This difficulty may be removed by a clever artifice. It was found out that in the case of one of the heaviest fluids of low vapour pressure, the so-called Thoulet's solution *, all droplets at first somewhat evaporated on reduction of the pressure around them to 200 mm. mercury. From this state of saturation, which was reached in about 40 minutes, the droplets remained constant for the duration of the observation (2 to 3 hours). The test bodies retained the mass assumed at the first reduction of pressure, also when the pressure about them was increased to atmospheric pressure. The following figure illustrates the evaporation and shows clearly the behaviour of the bodies described above. The time of observation is recorded as abscissa, a magnitude directly proportional to the mass as ordinate †. The extreme points refer to the corresponding second atmospheric pressure.

Fig. 1.



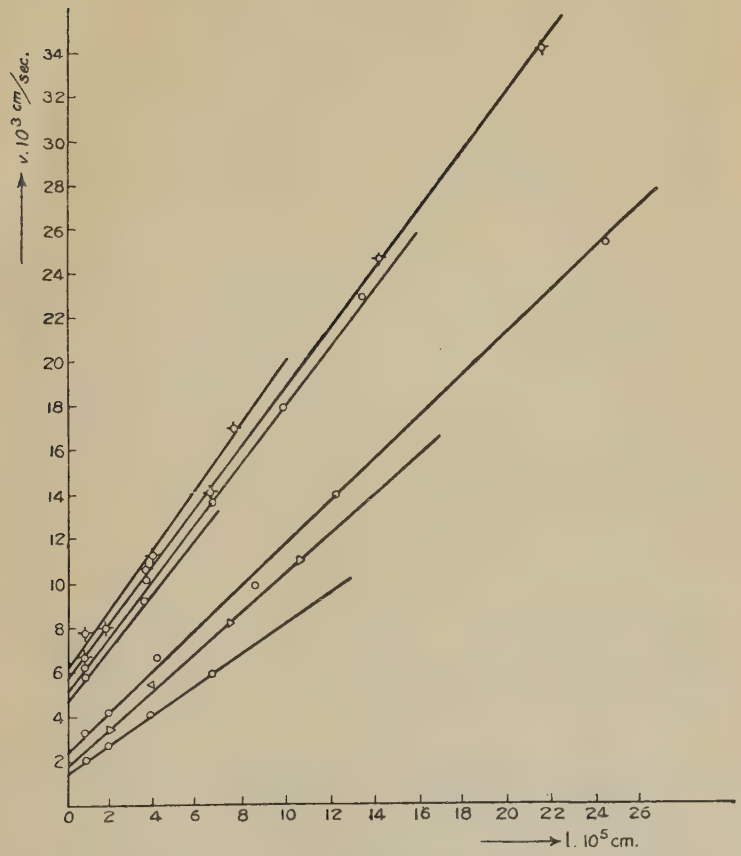
If we now measure the velocity of fall of the same test body at different pressures, returning the body after each measurement to its original position by means of the electrical field, we obtain an empirical relation between the velocities of fall and the corresponding gas pressures. In fig. 2 the mean free path of the molecules, l, which is inversely proportional to the pressure, is plotted as abscissa, the velocity of fall as ordinate. The figure shows that the velocity of fall increases with decreasing pressure. It moreover proves that the droplets are of various sizes, but

* The potassium-mercury-iodide ($K_4Hg_2I_4$) was sprayed in dry air. A nearly saturated solution of the density 3·012 was produced.

† This magnitude, the so-called balancing potential E*, is equal to $\frac{mg}{e}$ *i. e.* weight divided by the charge of the test body.

of the same density. If this were not the case, the curves (straight lines) would intersect. The straight lines, however, which represent the dependence of the velocity of fall upon the pressure, form a family of curves with parameter

Fig. 2.



equal to the radius a. If we now form the function $\frac{v}{v_0}=f\left(\frac{l}{a}\right)$ (v_0 = intercept in fig. 2), all points of this diagram fall upon a single curve, which is shown in fig. 3. In this way we have completed the proof that all test bodies have a

uniform density and that the measurements can be represented by a unitary law of resistance*.

§ 3. *Method of Computation.*

I. *Linear law of resistance.*—It has frequently been proved † that the velocity of small spheres in a resisting medium is proportional to the force acting :

$$v = \mathrm{B} \,.\, \mathrm{P}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the determination of the proportionality constant B we may resort to the theory of hydrodynamics. By means of Stokes's law we may substitute for B the expression

$$\mathrm{B} = \frac{1}{6\pi\mu a} \,.\, f\left(\frac{l}{a}\right), \quad . \quad . \quad . \quad . \quad . \quad (2)\ddagger$$

with the condition that the function $f\left(\frac{l}{a}\right)$ should become equal to 1 for infinitely small values of $\frac{l}{a}$, and thus gives the Stokes's law valid for fluids. It may be observed from fig. 2, that the dependence upon pressure is approximately a linear one. According to this we may next assume the function to be linear of the form :

$$f\left(\frac{l}{a}\right) = 1 + \mathrm{A}\frac{l}{a}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

From this together with (1) and (2), there results the corrected Stokes's law theoretically computed by Cunningham §. We then obtain :

$$v = mg \,.\, \mathrm{B}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

* The calculation procedure is here necessarily the same as that of J. Mattauch's cited paper on oil-drops of the magnitudes 3·5 to 11 . 10^{-5} cm.

† F. Ehrenhaft, *Ann. d. Phys.* lxiii. p. 782 (1920). Yu chen Yang, *Ann. d. Phys.* lxxvi. p. 333 (1925).

‡ The symbols used in the following formulæ mean respectively : B the mobility, *i. e.* the speed attained by the body under unit force ; "a" the radius of the body ; μ the coefficient of friction of the medium ; σ the density of the test body ; mg the weight, *i. e.* the product of the mass of the test body "m" and of the gravitational constant "g."

§ E. Cunningham, Proc. Roy. Soc. (A), lxxxiii. p. 357 (1910).

or according to (2):

$$v = \frac{1}{6\pi\mu a} \cdot \frac{4}{3}\pi a^3 \sigma g \cdot f\left(\frac{l}{a}\right), \quad . \quad . \quad . \quad (2a)$$

and finally, taking account of (3):

$$v = \frac{2}{9} \cdot \frac{\sigma g}{\mu} \cdot a^2 \cdot \left(1 + A\frac{l}{a}\right). \quad . \quad . \quad . \quad . \quad (4)$$

This can also be written in the form

$$v = v_0 + \beta l, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $v_0 = \frac{2}{9} \cdot \frac{\sigma g}{\mu} \cdot a^2$ and $\beta = \frac{2}{9} \cdot \frac{\sigma g}{\mu} A a$ *.

From this we determine for each separate drop the intercept v_0 and the slope β by means of the method of least squares. For each drop there are as many equations as points which lie upon the line. The density assumed known, the expression for v_0 gives us the radius of the test body, the expression for β the constant A of the law of resistance.

TABLE I.

Test body No.	$v \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	$v_0 \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	β.	$a \cdot 10^5$ cm.	A.	n †.
27	2·032	1·338	68·72	1·924	0·99	4
32	3·012	2·108	94·80	2·418	1·08	6
46	3·277	1·665	88·83	2·149	1·14	4
45	5·756	4·561	126·38	3·557	0·98	2
44	5·972	4·870	134·36	3·676	1·01	5
29	6·398	5·533	122·95	3·918	0·87	6
25	7·777	6·180	136·48	4·141	0·91	3

† n is the number of points for each line in the graph 2.

Table I. gives the corresponding values. The constants A, which we separately determined for each test body, lie all in the interval 0·9 to 1·1, and hence, with comparatively small deviations, within the theoretical limits. The assumption seems, therefore, plausible that a common law of resistance exists for all test bodies. This is shown by

* *Cf.* R. Bär and F. Luchsinger, *Phys. Zeits.* xxii. p. 225 (1921).

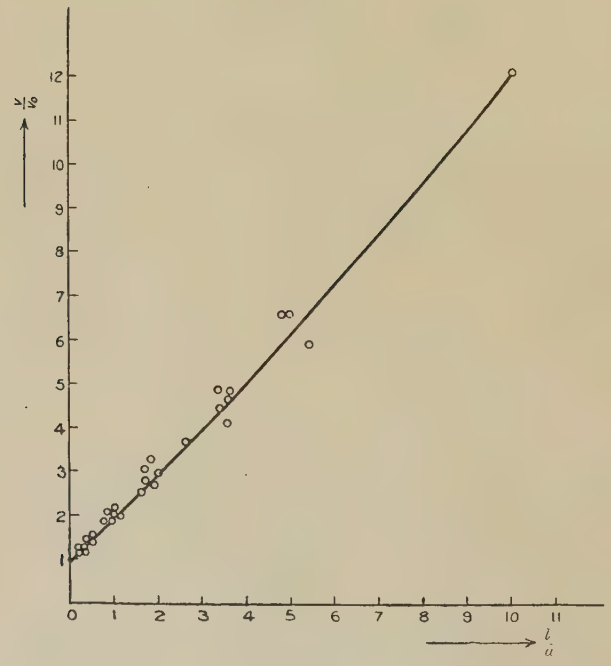
fig. 3. In this figure all points of the graph 2 have been brought upon a common curve by means of the relation

$$\frac{v}{v_0} = f\left(\frac{l}{a}\right), \quad \ldots\ldots\ldots \quad (6)$$

or according to (3):

$$\frac{v}{v_0} = 1 + A\frac{l}{a}. \quad \ldots\ldots\ldots \quad (7)$$

Fig. 3.



The slope of the line (7) gives the common constant A, which was likewise at first determined by taking the linear mean and which gave the value 1·04. The largest of the test bodies measured was of radius about $4 \cdot 10^{-5}$ cm., the smallest about $1{\cdot}9 \cdot 10^{-5}$ cm. The law of resistance, which until now had been proved valid only for larger spheres, hence retains its validity also for this order of magnitude.

§ 4. II. *Exponential law of resistance.*

In a well-known paper, M. Knudsen and S. Weber* determined empirically the mobility of large spheres in gas by means of vibration experiments. They obtained the following formula:

$$B=\frac{1}{6\pi\mu a}\left[1+\frac{l}{a}\left(A+De^{-C\frac{a}{l}}\right)\right], \quad . \quad . \quad . \quad (8)$$

to which F. Ehrenhaft has referred in his publication †. The question is, whether this formula is also valid for our fluid spheres, which lie at the extreme limit of visibility. For this purpose we write B in the form (8). We thus obtain a relation between $\frac{v}{v_0}$ and $\frac{l}{a}$:

$$\frac{v}{v_0}=1+\frac{l}{a}\left(A+De^{-C\frac{a}{l}}\right). \quad . \quad . \quad . \quad . \quad (9)$$

From the circumstance that the slight curvature is concave upwards, as can be seen from fig. 3, it follows that this three-constant formula agrees better with the results of observation. The computation was here carried out in the following manner. Approximate values were at first substituted for the constants A, D, C in formula (9). By this means the problem was reduced according to Gauss' method to the solution of linear equations. As many linear equations result as there are points in fig. 3. The corrected constants obtained in this manner are again substituted in equation (9), and the radii of the test bodies are computed according to Newton's method of approximation. The results are listed in Table II.

Table II.

Test body No. ...	27.	32.	46.	45.	44.	29.	25.
$a_e \cdot 10^5$ cm. ‖	1·962	2·470	2·176	3·574	3·650	3·789	4·212
$a_1 \cdot 10^5$ cm.	1·924	2·418	2·149	5·557	3·676	3·918	4·141

A=0·943. D=0·169. C=1·54.

‖ a_e marks the radius computed according to the exponential law of resistance, while a_1 is the radius determined by taking the linear mean.

We hence obtain:

$$B=\frac{1}{6\pi\mu a}\left[1+\frac{l}{a}\left(0{\cdot}943+0{\cdot}169e^{-1{\cdot}54\frac{a}{l}}\right)\right]. \quad . \quad (10)$$

* M. Knudsen and S. Weber, *Ann. d. Phys.* xxxvi. p. 981 (1911).

† F. Ehrenhaft, *loc. cit.*

If we now compare the results given in Table II. with the values obtained by taking the linear mean, we observe that the difference in value of the radii computed according to the two methods can be as great as 3 per cent. and in the mean does not exceed 1 per cent. According to this it is possible to compute with sufficiently good approximation the sizes of such small test bodies according to the Stokes-Cunningham's law, as has always been done.

§ 5. *The possibility of a Direct Determination of Magnitude.*

The observations were carried out with the illumination aperture 0·3 and the observation aperture 0·3 in an Ehrenhaft condenser with plates of diameter about 9 mm. These fluid droplets were perhaps the smallest which can be observed for the purpose of measurement with this optical apparatus. Mercury droplets might be rendered visible and observable in still smaller sizes, for they have a much greater coefficient of reflexion and, due to their greater density, fall much more rapidly. The problem of the validity of the law of resistance for colloidal mercury spheres is a matter for future experiment.

It would be particularly satisfying to be able to take out such a drop of fluid after observations, to place it upon a microscope slide, and to look at it with a microscope of the highest aperture by direct illumination. Essential difficulties stand, however, in the way. Such a precipitated droplet does not assume a spherical form, but a form computed by F. Neumann *. If we knew the capillarity constants of the fluid and of the glass, we might deduce the weight of the non-moistening drops from the measurements given by F. Neumann. But this procedure would also be hardly applicable to fluids. It, however, affords a means for the determination of magnitude and weight of solid bodies, and might permit of an extension of magnitude determinations by means of the law of resistance below the limits already approached.

§ 6. *Colloidal Gold in a Gas.*

It will then be found necessary to undertake the determination of the magnitude of smaller test bodies of radius less than $2 . 10$ cm.$^{-5}$. A very large field of modern physics is concerned with such particles. They are single, colloidal test bodies of a magnitude which runs from $2 . 10^{-5}$ cm. to $5 . 10^{-6}$ cm. and below. Up to the present time Ehrenhaft

* F. Neumann, Vorl. über d. Theorie d. Kapillarität, Leipzig, 1894.

has used purely optical methods for these test bodies *. These methods permitted of the computation of magnitude from the colour of the light scattered by the test bodies, assuming the optical constants of the test bodies as known. The choice of such test bodies is limited by several conditions. For the sake of an easier managing of the test bodies and of the shorter duration of the experiments, it is necessary to choose test bodies of great reflecting power and large density. Finally, we must choose test bodies which remain chemically invariable. Gold in nitrogen would offer a suitable material, as an occlusion or adsorption of the gas would in this case not be expected. F. Ehrenhaft has long ago referred to this selection of experimental material †.

The production of such test bodies can be undertaken in several ways. They can be produced either in an electrical arc between two gold electrodes of a thickness of 0·5 cm., or by heating finely divided gold powder in a quartz retort ‡. For the first we applied the later procedure. If, after heating, we pass the stream of gas through the condenser, we see the small gold test bodies as luminous points against a dark background. If many such particles are produced, it is observed that after a time several particles now and then meet and form a coagulum similar to that which is well-known in the case of fluids. We can, however, easily differentiate between the single and the complex particles. For whereas the single particles give rise to a normal diffraction disk §, the coagula are exceptionally brilliant, exhibit at first sight an irregular form and orient themselves in the electrical field so that the largest dimension falls in the direction of the electrical force. Every experienced microscopist would be able to distinguish the irregular test bodies, which now and then appear only after a considerable lapse of time. This he is able to do the more easily, if, under the same conditions of observation, he applies a larger aperture. In order to get the object plane in the centre of the condenser plates in this case, it is necessary to make use of a condenser of smaller dimensions, with condenser plates of diameter of but 3 mm. F. Ehrenhaft employed such a condenser in his first work. The test

* F. Ehrenhaft, *Phys. Zeits.* xv. p. 952 (1914); xvi. p. 227 (1915), etc.

† F. Ehrenhaft, *Phys. Zeits.* xii. p. 263 (1911).

‡ After a longer heating the retort gets covered within with a reddish sediment of the colloidal gold.

§ Discussion to the report of F. Ehrenhaft, *Phys. Zeits.* xi. p. 12 (1910) (Siedentopf).

bodies are clearly to be recognized as single particles also with this greater aperture. We of course wish to carry on our experiments only on these single test bodies, as the determination of the law of resistance has only in this case any meaning.

§ 7. *Comparison of the Gold Test Bodies with* $K_4Hg_2I_4$ *droplets, especially with reference to the Brownian Movement.*

We now wish to consider those smaller test bodies of radii below $2 \cdot 10^{-5}$ cm. Let us compare the $K_4Hg_2I_4$ test body no. 32, which, as is known, obeys the law of resistance, with a gold sphere such as referred to. It follows from Einstein's theory of the Brownian movement that the spheres which show the greater Brownian fluctuation have the greater mobility and hence the smaller radius *.

Table III.

$K_4Hg_2I_4$ test body no. 32. Times of fall in sec.

11·28	12·12	10·68	11·46	10·66	13·90	10·76	11·52	10·60	10·34
11·34	10·32	12·34	11·60	13·46	13·30	13·12	10·14	12·50	10·88

Distance of fall: $35{\cdot}0 \cdot 10^{-3}$ cm. $\overline{\lambda^2}$: $0{\cdot}978 \cdot 10^{-6}$.

Au test body no. 10. Times of fall in sec.

12·06	10·88	10·00	17·04	15·18	9·44	12·22	15·18	18·98	13·80
12·68	13·72	6·78	11·90	7·66	22·70	6·32	14·60	8·10	9·02

Distance of fall: $14{\cdot}5 \cdot 10^{-3}$ cm. $\overline{\lambda^2}$: $1{\cdot}963 \cdot 10^{-6}$.

If we now compare the figures given in Table III. for the two test bodies, we notice that the percent. fluctuation of the times of fall is 16·2 per cent. for $K_4Hg_2I_4$ and 51·0 per cent. for gold. The distance of fall of the gold test body is moreover more than half as small as that of the $K_4Hg_2I_4$ drop, from which it would appear that the Brownian fluctuation of the former should be yet smaller. If we determine the mean square displacement per second for the two test bodies, we find for gold the value $1{\cdot}963 \cdot 10^{-6}$, for $K_4Hg_2I_4$ the value $0{\cdot}978 \cdot 10^{-6}$, *i. e.* a value nearly twice as small as for gold. The result of computation that the Brownian fluctuation is in general much greater for gold particles than for $K_4Hg_2I_4$ droplets hence agrees with direct obser-

* According to Einstein's Theory: $B = \frac{N}{2RT} \cdot \overline{\lambda^2}$.

vations. Therefore the radius of the gold particle can at any rate be only as half as great as $2{\cdot}4 \cdot 10^{-5}$ cm.*

We may see, however, from the following circumstances that the Brownian movement can give no decision as to the question of the size of the test bodies. In the first place, let us assume that the possible number of single measurements is sufficient according to the statistical standpoint. One would then conclude that the Brownian movement leads to such important contradictions, that it would not be applicable for our computations. Let us then determine the mean square displacement per second, $\overline{\lambda^2}$, of the same test body at different gas pressures, and let us compute the product of the Loschmidt-Avogadro constant by the weight of the test body, $N \cdot mg$, separately for each pressure. We make use of the relation :

$$N \cdot mg = \frac{v}{\overline{\lambda^2}} \cdot 2RT, \quad . \quad . \quad . \quad . \quad . \quad (I)$$

where v is to be computed from the times of fall and $\overline{\lambda^2}$ from the deviations among them. For one and the same test body the values of $N \cdot mg$ would remain constant. In this connexion it was proved that the weight of the test body had not changed during the measurement †. The values for $N.mg$, however, show rather large fluctuations. For gold test body no. 12 we obtain for $N \cdot mg$ the following values :

Pressure in mm. Hg	751·0	242·3	159·0	751·0
$N \cdot mg\ 10^{-13}$	2·67	2·52	3·38	2·58

We notice that the value for $N \cdot mg$ at low pressure deviates about 26·5 per cent. from that at atmospheric pressure. At lower pressures these deviations are still much greater ‡.

In the second place, let us compute the mobility B in the well-known manner without assuming the density known according to Einstein's relation. If we then set this equal

* It may be noticed that the $K_4Hg_2I_4$ drops, as well as other particles of the same order of magnitude, which appear in their regular plane of vision as sharp luminous points against a dark background, are also well visible as spherical disks in the neighbouring planes of vision, which according to the size of the particles are more or less remote from each other. In the case of the observed gold test bodies this does not occur. These particles can be made visible only in the plane of distinct vision. This fact may also furnish the evidence that the observed gold test bodies are all smaller than the smallest of the $K_4Hg_2I_4$ drops.

† For this test body the balancing potentials E* (see note †, p. 32) are the following : 0·033, 0·030, 0·033, 0·035.

‡ S. Landman, *Z. f. Phys.* xxvii. p. 237 (1924).

to the mobility resulting from the law of resistance, we obtain:

$$B=\frac{N}{2RT}\cdot\bar{\lambda}^2=\frac{1}{6\pi\mu a}\left(1+A\frac{l}{a}\right) \quad . \quad . \quad . \quad (II)$$

In this manner we can determine the radius a. On the other hand, we can compute $N\,.\,mg$ according to (I). If we now assume that the test body is of spherical form (this can be proved by independent experiments, as will be discussed below), and set therefore

$$N\,.\,mg=N\,.\,\frac{4}{3}\,\pi a^3\sigma g,$$

we can compute the density σ by eliminating the radius from this expression by means of relation (II). If we compute the density of gold in this manner, we obtain for example for test body no. 10 the value 1·2. This result, when considered in conjunction with the proofs for the regular structure and form of the test body carried out further on in this paper, remains entirely inexplicable.

If we assume, however, that the possible number of single measurements is not statistically sufficient, we shall be able to draw no conclusions at all from the Brownian movement, and must leave it out of our computations.

§ 8. *The Law of Resistance for Colloidal Gold.*

We now wish to determine the law of resistance for these colloidal gold particles, and by this means their magnitude. The procedure of measurement and computation is here the same as that applied for $K_4Hg_2I_4$ and described in § 3 of this paper. The problem is indeed more difficult for gold, and because of the smallness of the test bodies cannot lay claim to the same exactness. In Table IV. we see that the radii correspond to the velocities of fall. We also notice the similarity between the diagram of fig. 4, where the velocities of fall are plotted as a function of the pressure (of the mean free path of the molecules, l), and the corresponding diagram for $K_4Hg_2I_4$. Hence we have also here to do with test bodies of the same density. If we now separately determine for each test body the constant A of the law of resistance according to the method given in the first part of this paper, we find the values given in Table IV. We notice, however, that these constants are much smaller than those for $K_4Hg_2I_4$. Thereby we have made use of the normal density of gold.

Fig. 4.

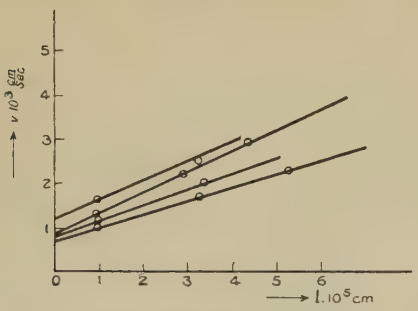


Table IV.

Test body No.	$v \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	$v_0 \cdot 10^3 \frac{\text{cm.}}{\text{sec.}}$	β.	$a \cdot 10^5$ cm.	A.	n.
14	0·957	0·711	30·35	0·54	0·23	3
10	1·167	0·811	35·78	0·58	0·25	3
12	1·308	0·870	46·38	0·60	0·32	5
7	1·404	0·881	32·50	0·61	0·22	4
1	1·633	1·293	36·36	0·73	0·20	2

The radii of the gold test bodies are of the colloidal order of magnitude, as has been made plausible by consideration of the Brownian movement. The matter hence takes on an appearance, as if the law of resistance were different for small metallic colloidal test bodies from that for large drops of fluid. We reserve, however, our definite opinion about this matter until we are able to make use of sufficiently great statistical data of other metallic colloidal particles.

Some writers have tried to argue in the reverse way. For, if we consider the density σ as unknown, there are three unknown qualities a, A, σ, present in the two equations (4) and (5). If we then assume the density σ as known, we may compute the radius a and the constant A *. This has been carried out in Table IV. One can, on the other hand, take the value of A from the results obtained from other test bodies, *e. g.* $K_4Hg_2I_8$, and thus determine σ. The result of this method of computation is, however, very improbable. We find in this manner, viz. for gold densities up to 1, *e. g.* for the gold test body no. 10, mentioned above, a density $\sigma = 1{\cdot}7$ and a radius $1{\cdot}95 \cdot 10^{-5}$ cm. The question

* F. Ehrenhaft, *Ann. d. Phys.* lxiii. p. 784 (1920). Th. Sexl, *Ber. d. Akad. d. Wiss.* (II *a*), cxxxii. p. 139 (1923).

remains unanswerable, why the single particles of colloidal gold should have a density deviating from that of gold in the bulk.

§ 9. *Capture and Microscopical Observation of the Single Gold Test Body.*

For the purpose of the direct determination of magnitude we now wish to apply the above-described method, which is invalid for fluids, to gold. The applicability is dependent upon the success of making observations of such a single test body of gold, of the isolating it and of examining its form and structure by means of the direct microscopic image. This has for the first time been successfully accomplished. A single test body of the size $5 . 10^{-6}$ cm. and of weight approximately $1 . 10^{-11}$ was observed in the condenser, taken out and measured directly. The following means were employed for this purpose.

A brass cylinder is jointed to an Ehrenhaft condenser with plates of diameter 9 mm. By means of a micrometer-screw a pin can be thrust within. The entire apparatus is made vacuum proof. On the front of the pin there is a small silver leaf of the thickness 0·06 mm., which has in the centre a finely bored hole. A thin piece of glass or quartz of the thickness about 0·1 mm. is fastened below this hole.

At first the test body is put through the usual measurements. the silver leaf is then with the greatest care thrust horizontally within the condenser by means of the micrometer-screw. In order to make the experiments possible we must earth the leaf. The test body is now drawn into the space above the hole of the silver leaf by means of the divided upper condenser plate, which can be brought to another potential at the centre. The particle is then exactly centred and allowed to fall through the hole of the silver leaf upon the piece of glass *. It was frequently impossible to find the single test body on the glass. We often succeeded, however, in throwing a single test body upon the centre of the leaf. When we then took out the leaf and examined it with the dry aperture 0·95, we found the test body sought, but also a second or a third. These other particles are from other planes of vision and fall upon the leaf without being observed during the fall. All these test bodies were nearly of the same size. After they had been located with the dry aperture 0·95, they were examined in direct light and against a dark background with oil-immersion aperture 1·3. They

* The cleaned cover-glass was of course microscopically examined with aperture 0·95 before the experiments and found free from particles.

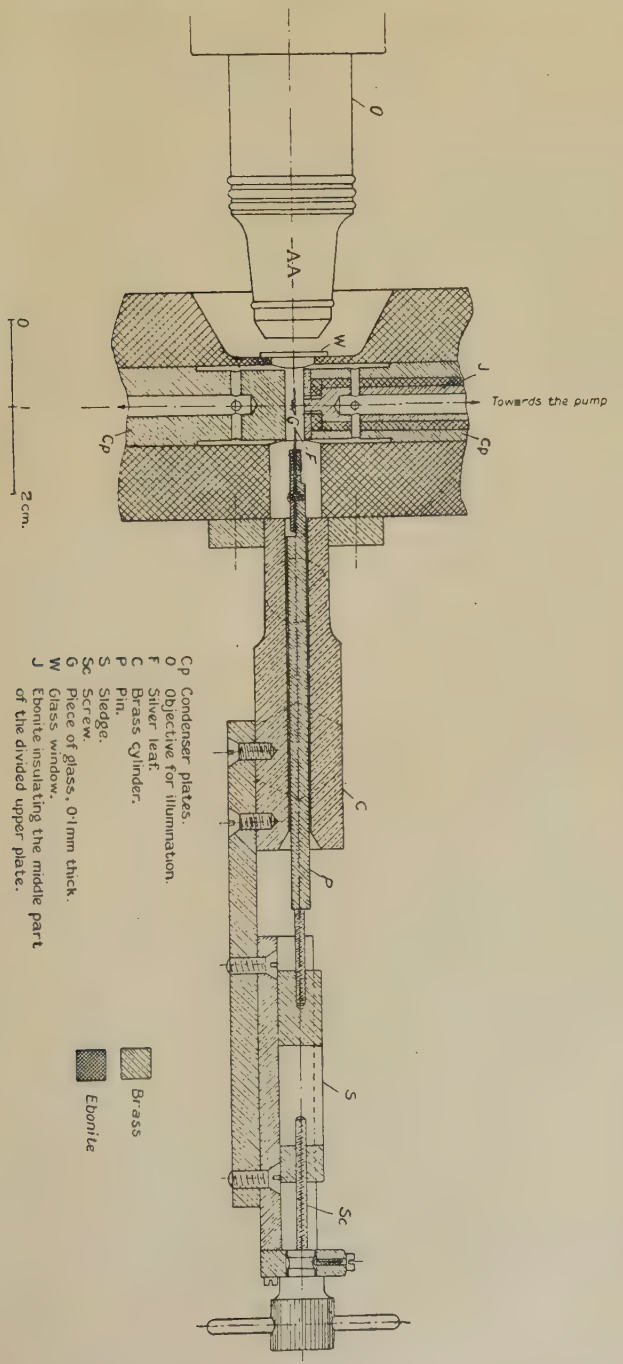

O
AA
W
J
Towards the pump
Cp
Cp
F
C
P
S
Sc
0
2 cm.
Cp Condenser plates.
O Objective for illumination.
F Silver leaf.
C Brass Cylinder.
P Pin.
S Sledge.
Sc Screw.
G Piece of glass, 0·1 mm thick.
W Glass window.
J Ebonite insulating the middle part of the divided upper plate.
Brass
Ebonite

Fig. 5.

then exhibited an isodiametrical form, which appeared dark against a light background and light against a dark background. "As is well known, the action of a microscope for such single particles of any kind may be compared with that of the telescope by the observation of fixed stars. These sorts of objects are always made visible, even if the diameters are less than one-tenth of the wave-length. Their visibility depends among other things upon the light contrast, and for weak shadow effects particularly upon the sensitiveness of the retina of the observer's eye. When the size of the object is appreciably less than a multiple of the wave-length, the diameter and the form of the image are no longer completely determined by the diameter and the form of the object, but depend upon the numerical aperture and upon the wave-length" *. For the distance between two points which may still be resolved in the extreme case is $\frac{\lambda}{2A}$, where λ is the effective wave-length, and A the aperture. We could in fact observe this. For when we microscopically examined one of these test bodies with the aperture 0·95 and attempted to determine the apparent radius, we found *e. g.* a value about $1{\cdot}5 \cdot 10^{-5}$ cm. When we now examined the same test body in oil-immersion, we found for the radius a value of 0·9 to $1 \cdot 10^{-5}$ cm. However, even with this aperture the test body did not appear to be fully resolved, but it seemed as if it would be found to be smaller, if we made use of a greater aperture. We could, namely, not yet obtain a sharp image with this aperture †. "For such isodiametric or nearly isodiametric particles always appear as nearly circular disks of diameter $\frac{\lambda}{2A}$, as soon as the actual diameter in all directions is appreciably smaller than this quantity. This behaviour occurs without exception, whether the objects in question appear as light particles against a dark or a less transparent background, or as dark particles against a light field." We could attain both effects by the adjustment of the iris diaphragm.

The findings would therefore indicate, as we worked with visible light, that the test bodies were in any case of radius less than $1 \cdot 10^{-5}$ cm. If there were a greater aperture for visible light we could actually measure the diameter of the test body. We notice that the microscopic examination

* L. Dippel, *Handb. d. allg. Mikroskopie*, ed. ii. p. 317 (1882).

† We worked also with the aperture 1·3 with fixed dark field diaphragm.

of the test body at least furnishes an upper limit for the radius. If we now assign a density 1 to 1·5 to such test bodies, the radius would come out twice as large as the limit indicated by the optical findings.

§ 10. *Ultraviolet Photographs of Colloidal Gold.*

We must, however, admit that this question can only then be fully cleared up, when we obtain photographically a real image of the test bodies. This has also been successfully accomplished.

Prof. A. Köhler with C. Zeiss in Jena has, as is known, constructed, according to the computations of v. Rohr, quartz monochromatic microscope objectives of the aperture 1·25, which permit of microscopic photographs of the finest structures. As the resolving power of the microscope increases in proportion as the effective wave-length decreases, we may by applying the greatest aperture 1·25 and ultraviolet light of the wave-length 275 $\mu\mu$ still resolve two points at a distance $1{\cdot}1 \,.\, 10^{-5}$ cm. On account of the short wave-length of the ultraviolet light the resolving power becomes as great as the relative resolving power of an aperture 2·50 by daylight. Such an aperture it is impossible to produce with our present means to-day.

One of the writers had such ultraviolet photographs made in our institute. Photographs were at first taken of the algæ "*Surirella gemma*" and "*Pleurosigma angulatum*" with the magnesium line (I. & II., Pl. I.). We will call attention to the comparison of these photographs with that by visible light*.

Prof. A. Köhler in Jena had the kindness to take ultraviolet photographs of small selenium spheres, which Mr. H. Kaiser had produced in Jena according to the Ehrenhaft method. The spheres were let fall upon a quartz plate and immersed in glycerine; the photographs were made with a monochromatic objective of focal length 1·7 mm. and the numerical aperture 1·25 (magnification 1500). From the photographs we see at once that these test bodies retain the spherical form also in submicroscopic sizes †.

* F. Ehrenhaft, *Wien. Akad. Ber.* cxxiii. [II *a*], January 1914.

† We wish to express the warmest thanks to Prof. A. Köhler for his production of these photographs. He applied an arc of length 3·5 cm., an alternating current transformer of from 200 volts to 10,000 volts and a condenser of 2 . 10,000 cm. capacity. The potential across the primary of the transformer was 100 volts, the primary current 2·5 A., the source potential 200 volts, and the frequency 50. Current and potential were measured with hot-wire instruments. The ultraviolet light was concentrated by means of a quartz condenser of four lenses with duplex front lens.

Mr. E. Sax * was then induced to produce similar photographs in our institute in Vienna. These photographs also show an exact spherical form. We reproduce the photographs here (IV., Pl. I.), because definite experiments on radioactive Se test bodies were described in Phil. Mag. †, and reference made to the prospective proof of the spherical form.

The photographs of colloidal gold particles (V., Pl. I.), which had been let fall upon a quartz plate and resolved, demand particular interest. For the sake of comparison the Zeiss scale 10^{-3} cm. per division was photographed on the same plate. We notice that all these test bodies are of a colloidal order of magnitude of radii from 5.10^{-6} cm. to 1.10^{-5} cm. and possess the spherical form. A single colloidal test body was also photographed. The radius found by these means was 7.10^{-6} cm., which is in a good agreement with the results from the law of resistance and from the direct optical findings ‡. We may indeed consider the opinion so often expressed that such test bodies do not possess a spherical form as refuted.

Mr. E. Sax has recently succeeded in taking photographs of mercury spheres by means of the ultraviolet light with the wave-length $\lambda = 275\,\mu\mu$. The same spot of the preparation with large and small spheres was resolved by varying the planes of vision, the distance between them being removed to 5.10^{-5} cm. from each other. We would like to draw attention to the different sharpness of the images of the differently sized spheres of radii from 5.10^{-6} cm. to 5.10^{-5} cm., as shown in photograph VI. (Pl. I.). The group (1) on the left corresponds to the lowest plane of vision. Each following group corresponds to about 5.10^{-5} cm. higher plane of vision, being attained by turning the micrometer-screw of the microscope. It should be interesting to compare these series of spherical mercury dorps with the photograph VII. (Pl. I.), which shows non-spherical particles of sulphide of antimony, taken up with the same optical means as the mercury drops.

* Our thanks are due to Mr. H. Kaiser, teacher of the "Graphische Versuchsanstalt" in Vienna, and to Mr. E. Sax, cand. phil., for the production of these photographs. The apparatus used in the production of these ultraviolet photographs was similar to that of Prof. A. Köhler. They used the same length of arc, an alternating current transformer of from 110 volts to 10,000 volts, and a condenser of the same capacity as that of Köhler. The potential across the primary was 43 volts, the primary current 5·6 amperes, the source potential 110 volts, the frequency 45.

† *Loc. cit.*

‡ In the original photographs the test bodies are shown so small that a reproduction in a journal would hardly be possible. Mr. H. Kaiser had the kindness to enlarge the photographs about three times, so that the enlargement of the test body is 4300 times.

In the former paragraph we have deduced the fundamental facts concerning the resolving power of the microscope at the limit of the visibility of light, and have made reference to the quoted passages of Dippel's Handbook. It should be emphasized beyond this that the argumentation, concerning the limiting power of the microscope, is carried out in this book under the assumption that, besides the chief maximum, only one neighbouring maximum of the light diffracted by the small body co-operates in the production of the images *. By these means is attained only the so-called "lowest degree of similarity." The microphotographs produced by means of ultraviolet light, however, show that the difference of the form between the spheres (selenium, gold, mercury) and the non-spherical particles (sulphide of antimony) is given very well also to this order of magnitude.

In order to make the state of affairs perfectly clear, we wish to call attention to the following circumstances. All single particles of colloidal gold, for which the law of resistance was determined by evacuation, give for the constant A a value 0·2–0·3. All the test bodies removed from the condenser were isodiametrical and of order of magnitude below the limit which can still be measured by means of the aperture 1·3 in visible light. Finally all test bodies when photographed with ultraviolet light showed an exact spherical form. The measurements made on the ultraviolet photographs, which represented the real images of the test bodies, give the same colloidal magnitude, which, as mentioned above, follows from the law of resistance. It is a matter for the future to carry out these somewhat difficult and extremely tedious experiments on the same test body.

We may therefore be sure that our assumption of the spherical form is the correct one, and that we must draw the conclusions following from this assumption and from the normal density of the test bodies.

The University of Vienna,
November 14, 1925.

Appendix.

The fact that a regular law of resistance is found on drops of the "Thoulet"-solution is not isolated, as has been shown by the further experiments in our institute. The law of resistance has since been empirically determined on drops of

* *Cf.* E. Abbe, 'Die Lehre von der Bildentstehung im Mikroskop,' p. 95, Braunschweig, 1910.

a saturated solution of $BaHgI_4$, by means of the same procedure as that on $K_4Hg_2I_4$-drops. By concentrating the solution of $BaHgI_4$ to the state of complete saturation, it could be reached that the test bodies retained the constancy of the mass also at the lowest gas-pressures. Mr. M. Reiss has established the law of resistance for this fluid of the density 3·5 by means of a sufficiently great number of points (130 points, according to diagram 3 of this paper) *.

Not only the sprayed fluid-drops, however, furnish a unitary law of resistance, but also selenium spheres produced by evaporation, the ultraviolet photographs of which we have previously shown. This law for selenium has been set up by Mr. H. Trebitsch in our institute by calculating the results of the observations taken by J. Mattauch. On solid selenium spheres about the same law results, as on the drops of fluids. The twice-repeated computation according to the method of least squares gives for constants of the exponential law of resistance the following values: $A=1{\cdot}034$, $D=0{\cdot}172$, $C=2{\cdot}77$ (conf. equation 10). All these substances of various densities, *i. e.*, oil (0·93), $K_4Hg_2I_4$ (3·01), $BaHgI_4$ (3·50), Se (4·26), therefore give approximately the same relation for the mobility as was obtained quite independently of any assumption concerning the charges of the test bodies.

The problem of the validity of the law of resistance on these test bodies of the order of magnitude to 1.10^{-5} cm. is hence solved. It requires, however, some further examination on metallic test bodies of radii below 1.10^{-5} cm. to 5.10^{-6} cm. For the methods which are to be undertaken in this case we refer to the communication, "Sur l'observation et la mesure des plus petits aimants isolés," which has appeared in the *Comp. Rend.* vol. 182, p. 1138. Paris, 1926.

The *electrostatic charges* of these test-bodies, computed with the law of resistance that has been determined in a purely mechanical way, are especially remarkable. The results obtained on the drops of the $BaHgI_4$-solution of radii from 1·2 to $3{\cdot}2.10^{-5}$ cm., as well as on selenium spheres of radii from 1·2 to $3{\cdot}5.10^{-5}$ cm., are still more conspicuous than that on the drops of the $K_4Hg_2I_4$-solution (the charges of the $K_4Hg_2I_4$-drops treated in this paper are the following: 4·34, 3·82, 3·75, 5·12, 4·88, 22·82, $10{\cdot}26.10^{-10}$ E.S.U.). Among 20 charges measured directly on the $BaHgI_4$-drops, 13 were found to be smaller than $4{\cdot}0.10^{-10}$ E.S.U.; among 26 charges on selenium spheres 8 are deviating from the electron by more than 20 per cent., the smallest charge being measured to $2{\cdot}80.10^{-10}$ E.S.U.

* The constants of the law of resistance are in this case: $A=0{\cdot}879$, $D=0{\cdot}229$, $C=2{\cdot}61$.

The extensive tables and proofs regarding this communication will be published in the *Zeitschr. f. Physik* in a short time. The objection so often expressed against these charges, that the carriers of them were non-spherical particles of irregular density, can evidently not be made in this case.

By this the problem of the determination of the charges of single small spheres, which has been discussed in the literature of the last 17 years, has been brought to a conclusion.

Vienna, May 18th, 1926.

IV. *The Loud-Speaker as a Source of Sound for Reverberation Work.* *By* A. H. Davis, *D.Sc.*, *and* N. Fleming, *B.A.*, *Physics Department, The National Physical Laboratory**.

Abstract.

In reverberation work it is important to have a source of sound of which the activity can be varied in a large known ratio. The suitability of a loud-speaker for this purpose has been studied. A loud-speaker actuated by audio-frequency current of pure sine wave form was set up in a room, and measurement was made of the manner in which the intensity of sound at any point in the room varied with the exciting current. The measurements of relative sound intensity were made by means of a condenser microphone with suitable accessory apparatus for measuring the small electromotive forces involved. An electrodynamic type of loud-speaker was found to be satisfactorily constant and free from lag, and over a wide range to have an activity approximately proportional to the square of the exciting current. An electromagnetic instrument tested was, on the whole, less satisfactory. As a further test, measurements were also made of the rate of decay of residual reverberant sound in each of two large rooms, using the loud-speaker as source. The instrument proved convenient in operation, and satisfactory results were obtained. The logarithmic law for the decay of reverberant sound in rooms was established over an intensity range which appears to be about 3000 times as great as that used by W. C. Sabine in directly testing its validity.

IN reverberation work, where the rate of decay of sound in a room is estimated from measurements of the duration of audibility after the source has ceased, it is fundamentally necessary to conduct experiments with

* Communicated by the Authors.

different values of the initial average intensity in the room. In determining the initial reverberant condition of a room—whether auditorium or test-chamber—this measurement is unavoidable. In cases where the acoustic condition of the room is altered in any way—say by the introduction of absorbing materials for test—the changed interference system in the room may alter the output of the source. Consequently, it is not sufficient merely to observe the altered duration of audibility for a single condition of the source, but strictly a repetition of the multiple intensity work is necessary. It is thus important to have a source of sound of which the activity can easily be varied in a known ratio, and it is desirable, in order to obtain accurate measurements, that this ratio should be large. Sabine * used a number of similar organ pipes, but obviously no great range of intensity is attainable by such means unless the number of pipes is inconveniently large. Moreover, Sabine † found that, unless his pipes were placed at a considerable distance apart, they reacted upon one another, and the total activity of n pipes was by no means n times the activity of one sounded alone.

Experiments have been carried out to determine the suitability of a loud-speaker as a source of sound in reverberation work, for with a single instrument of this type a great range of activity is readily obtained by varying the current through its coils. For a given position in the room and for a given wave-length the acoustic impedance of the space into which the loud-speaker operates is fixed. Under these conditions, with a satisfactory instrument, the activity will remain constant for a constant current input, and for simplicity it is desirable that the activity be proportional to the square of the current.

I. Study of the Loud-Speaker as a Source.

Method of Experiment.

If a source of sound of constant frequency is placed in a closed room, a stationary system of waves is set up which remains fixed so long as the wave-length remains constant. The sound intensity varies from point to point in the room, but at any one point it remains constant

* Sabine, 'Collected Papers,' Paper No. 1, Harvard Univ. Press, 1922.
† Sabine, *loc. cit.* See also p. 83.

for a source of constant activity. If, as is usually assumed, the energy absorbed on reflexion by the walls is always directly proportional to the intensity of the incident sound wave, and unless any degradation of sound energy into heat in the air itself is more pronounced for loud sounds than for feeble ones *, the intensity at any point in the room will be directly proportional to the activity of the source.

In the present experiment a loud-speaker was used as the source of sound, and a microphone, placed at some other point in the room, served to measure the relative values of the intensity set up at that point. Measurements were made both with an electromagnetic loud-speaker and with one of electrodynamic type. Three types of microphone were used, working respectively on electrostatic, electromagnetic, and electrodynamic principles. The e.m.f. generated by the electrostatic microphone is, for small amplitudes, directly proportional to the amplitude; the sensitivity varies little with time and, in particular, the variation with temperature is quite negligible †. With the other two types for small amplitudes the e.m.f. is directly proportional to the velocity of the diaphragm and therefore, in general, to the pressure in a harmonic sound wave. Thus, in all cases the e.m.f. gives a measure of the sound amplitude at the position of the microphone.

Apparatus.

A diagram of the apparatus used is given in fig. 1. The oscillatory current to actuate the loud-speaker S was generated by a valve oscillator P, and amplified and purified by the tuned amplifier Q, which consisted of four valves of the L.S. type, connected in parallel. The loud-speaker circuit, which contained a thermal milliammeter A_1 and a rheostat R, was inductively coupled to this oscillator unit. A low-resistance (120 ohm) loud-speaker was used, and it was possible to obtain currents of more than 100 m.a. r.m.s. at all frequencies from 125 to 2000 vibrations per second. The wave form of the current was investigated by means of a cathode ray oscillograph, and in all cases a pure sine wave was

* It is generally believed that very loud sounds such as those from fog-horns, etc., suffer very pronounced degradation. Hart (Roy. Soc. Proc. cv. p. 80 (1924)) in the case of sound of very low frequency (100) claims to have measured appreciable degradation of this type at much feebler intensities. This conclusion has not yet been confirmed.

† Wente, Phys. Rev. x. p. 39 (1917); Phys. Rev. xix. p. 498 (1922).

obtained at each frequency throughout the range of currents employed.

The microphone T was connected—via a connexion unit C in the case of the electrostatic type—through a two-way switch K to the input of the amplifier system U.V. The output of the amplifier system was connected through an iron core transformer to a vacuo junction and galvanometer G. A galvanometer deflexion was thus obtained, the magnitude of which was a measure of the small e.m.f. generated by the microphone.

Fig. 1.

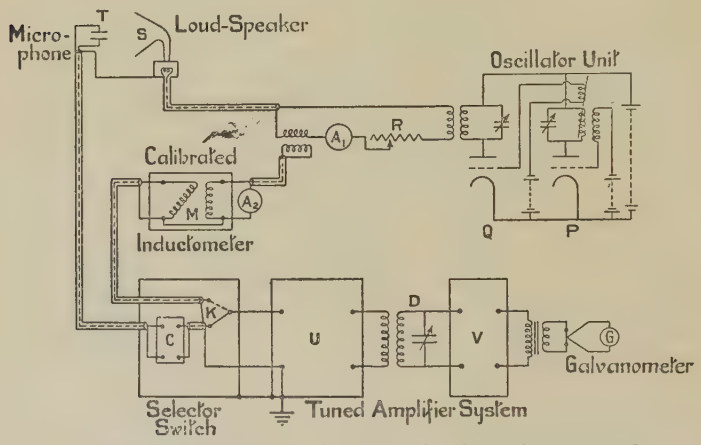


Diagram of arrangements for measuring intensity of sound from loud-speaker.

To determine the actual value of this e.m.f. a substitution method was adopted. By means of the key K a known variable e.m.f. from the mutual inductometer M could be substituted for that from the microphone, and its magnitude could be adjusted until an equal galvanometer deflexion was obtained. The current through the primary circuit of the inductometer was measured by the milliameter A_2, and was obtained by inductive coupling to the main loud-speaker circuit: in consequence of this arrangement, the two equal e.m.fs. from microphone and inductometer respectively were identical in frequency, and the characteristics of the amplifier system UV were thus eliminated. The amplifier system was nevertheless carefully constructed, and was composed of resistance capacity units designed to deal faithfully with the inputs obtained.

Precautions were taken to avoid leaks, and to suppress electromagnetic and electrostatic interference from outside sources. The oscillator was situated as far as possible from the rest of the apparatus, and its coils were so oriented that their electromagnetic fields were without effect upon the measuring system. The sharply tuned circuit D in the amplifier system helped to filter out leaks arising from extraneous sources. This amplifier system and its input switch etc. were screened in metal boxes, and leads to the amplifiers from the microphone and inductometer were shielded. Indeed, the whole of the amplifier and all leads to the grid of the first valve could be regarded as enclosed in the leads to the earthed filaments of the valves. The leads to the loud-speaker were shielded and, with the case of the loud-speaker, were suitably earthed. With these precautions leaks were reduced enormously : the slight residual leak, equivalent in general to an input of the order of 10 micro volts, was usually quite negligible.

Experimental Procedure.

Very early in the work it was found to be vitally necessary to keep the frequency constant in order to avoid any shift of the interference system in the room, and the consequent change in the intensity at the position of the microphone. Great care was therefore taken of this point, and the frequency was tested and adjusted, if necessary, before each reading. But, even though the frequency remain constant, the interference system will change if the temperature of the room varies, since the velocity of sound, and therefore its wave-length, varies with the temperature. In testing the constancy of a loud-speaker over a considerable period the temperature of the room should therefore be kept constant. It was not possible, however, to control this temperature, but some idea of the magnitude of the change to be expected from change of temperature was obtained by altering the frequency by an appropriate small amount. To eliminate the effect of any such temperature drift when measuring the proportionality of loud-speaker output to exciting current, readings for a standard current were taken alternately with the readings for other currents.

Results.

Let i and i' be respectively the current through the loud-speaker and that through the primary of the standard

mutual inductance. Since the coupling between these two circuits is fixed, at any given frequency i' is proportional to i, and we may write

$$i' = k_1 i.$$

Corresponding to the loud-speaker current i, let a be the sound amplitude at the position of the microphone, E the e.m.f. generated by the microphone, and M the reading of the mutual inductance when a balance is obtained.

Further, let a_0, E_0, M_0 be values corresponding to a standard current i_0. Since the e.m.f. generated by the microphone is equal to that applied to the amplifier from the secondary of the standard mutual inductance, we have for a frequency n $(=\omega/2\pi)$,

$$E = M\omega i' = M\omega k_1 i,$$

whence

$$\frac{E}{i} = M\omega k_1.$$

If the e.m.f. generated by the microphone is proportional to the amplitude of the sound which excites it, we may then write

$$\frac{a}{i} \propto M\omega k_1$$

or

$$\frac{a}{i} = k_2 M. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the standard value of the current this becomes

$$\frac{a_0}{i_0} = k_2 M_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Choosing arbitrary units so that the sound amplitude per unit current is unity for the standard current, *i. e.* putting $k_2 = \frac{1}{M_0}$,

we have

$$\frac{a}{i} = \frac{M}{M_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If the acoustical activity (energy units) of the loud-speaker is proportional to the square of the exciting current, the sound amplitude at the microphone should be proportional to the loud-speaker current. Consequently,

in this case, provided the microphone e.m.f. is proportional to the sound amplitude, $\frac{M}{M_0}$ should remain constant and equal to unity as the loud-speaker current is varied.

Preliminary tests.—If the condition of simple proportionality is satisfied by the microphone, it is to be expected that the form of relation between M/M_0 and i will be the same whether it is obtained with the microphone close to the loud-speaker, in a position of relatively high intensity, or at a distance in a position of relatively low intensity. Experiments were therefore conducted at a frequency of 500 vibrations per sec. with the microphone in different parts of the room in positions of widely differing intensity.

When an ordinary electromagnetic telephone receiver was used as a microphone it was found that in positions of high intensity the value of $\frac{M}{M_0}$ fell off considerably for high currents, whereas in positions of low intensity the fall was not nearly so pronounced. An electrodynamic type—actually part of a commercial loud-speaker movement—also gave different curves in different parts of the room, but in this case the value of $\frac{M}{M_0}$ fell off for low values of the loud-speaker current. The magnitude of this effect could be decreased by more accurately centreing the coil between the magnetic pole pieces and, though the commercial instrument used could not be made quite satisfactory, it is possible that a precision instrument of this type would be.

The condenser microphone, however, showed no such changes. The curves obtained in five different positions in the room, varying from 1 inch in front of the mouth of the loud-speaker horn to over 8 feet away, did not vary from the mean by more than the experimental error.

This result is also of interest in its bearing upon the question of degradation of sound of the type studied by Hart*. If, at this loudness and frequency, such degradation were appreciable, the values of $\frac{M}{M_0}$ should fall off for the higher currents more when the microphone is at a distance from the loud-speaker than when it is close to the mouth of the horn. Since no such behaviour was shown, although the range of intensities used was much greater than that

* Hart, Proc. Roy. Soc. cv. p. 80 (1924).

used by Hart, it must be assumed that at this frequency, at any rate, there is no appreciable degradation.

In obtaining the results given below the condenser microphone was always used. Since it is less sensitive than the other types, it was placed close to the mouth of the loud-speaker horn to increase the accuracy of the readings for the low values of the loud-speaker currents.

Electromagnetic type of loud-speaker.—When the loud-speaker current was first switched on the amplitude of the sound emitted from the electromagnetic instrument did not immediately assume a steady value, but continued to increase for some time. This effect was more marked with high currents, as long as twenty minutes being necessary before the increase became imperceptible. When this state had been reached stopping the current for a few seconds did not result in a return to the original condition. The phenomenon appears to be due to the local heating effect of the current in the coils of the loud-speaker, which may result in the pole pieces being brought closer to the diaphragm and so give an increase of efficiency.

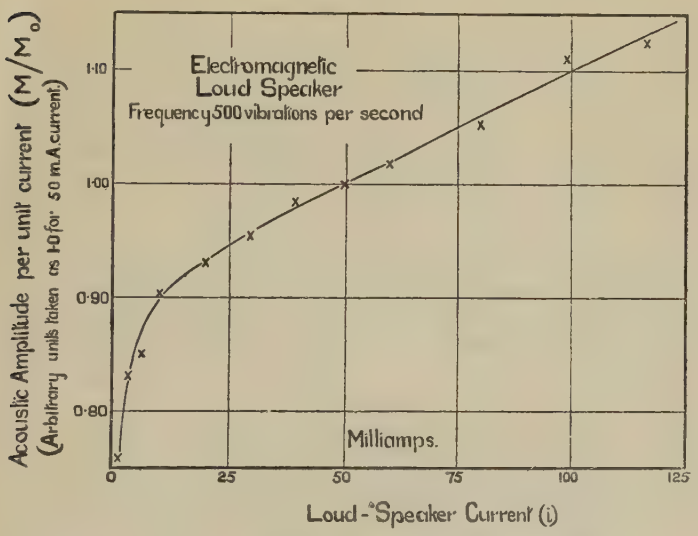
This heating effect was again apparent when the effect of altering the loud-speaker current was studied. On changing to a high current from a low one the efficiency was at first unchanged, but rose gradually for some time ; the opposite effect occurred when the current was again reduced.

Usually throughout any period of several hours, during which the current remained constant, the temperature of the room rose and the sound amplitude at the microphone drifted continuously, the sign of the drift being dependent upon the position in the room. The effect was almost competely explained in sign and magnitude by the shift of the interference system in the room, due to the effect of temperature upon wave-length. After allowance was made for this, there was a very slight residual effect representing a decrease of efficiency of the loud-speaker when its general temperature was raised.

The curve finally obtained for the relation between the loud-speaker current and the sound amplitude per unit current, for a frequency of 500 vibrations per second, is given in fig. 2. It shows that the efficiency increases with the current. The very pronounced fall indicated for very low currents is in a region where measurement was difficult, and where small leaks to the amplifier may have become appreciable. Nevertheless, it is thought to be real.

Owing to the long time taken by this loud-speaker in settling down to a steady output, it does not seem very suitable for reverberation work. Further, the increased efficiency at high current strengths, while not of any importance in the normal working of a loud-speaker, is too great for the instrument to be completely satisfactory for the special purpose in view.

Fig. 2.



Relation between loud-speaker current and acoustic amplitude per unit current. (Electromagnetic loud-speaker.)

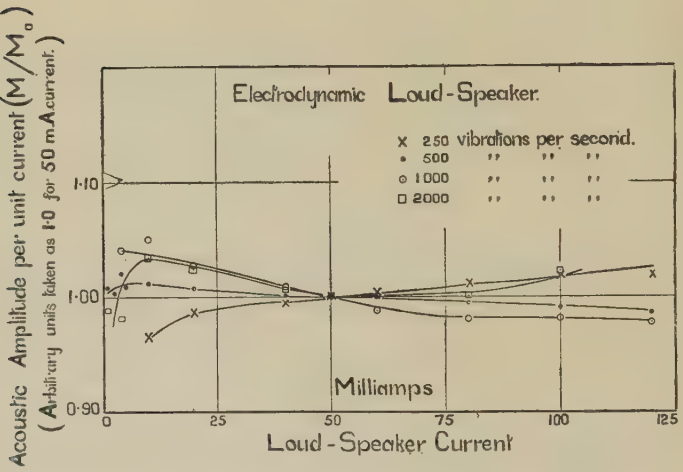
Electrodynamic type of loud-speaker.—The electrodynamic loud-speaker was of the type in which a coil of wire attached to a diaphragm moves in the field of an electromagnet. For constancy it was naturally necessary to maintain the current through the field coils of the magnet at a constant value. A ten per cent. change in current strength resulted in a five per cent. change in the estimated sound amplitude.

As a loud-speaker the instrument assumed its final steady output immediately the audio frequency input was supplied. In any long series of readings for a constant value of this input, the sound amplitude at the microphone drifted continuously since the temperature of the room did not remain constant. With this instrument the drift

appeared to be due almost entirely to shift in the interference system in the room arising from the changed temperature. Certain irregular variations from the general drift, of the order of 1 to 2 per cent., were due most probably to very slight errors in tuning.

The curves given in fig. 3 show the relation between

Fig. 3.



Relation between loud-speaker current and acoustic amplitude per unit current *. (Electrodynamic loud-speaker.)

the current and the sound amplitude per unit current (M/M_0) for four different values of the frequency. Again there is evidence of falling off in the efficiency for very low currents though, as above stated above, the measurements in this region are least reliable. Throughout the wide range of currents employed, however, the maximum variation of $\frac{M}{M_0}$ is only $2\frac{1}{2}$ per cent. in the best case ($n=500$) and 6 per cent. in the worst ($n=250$). It may be shown that the error introduced in reverberation

* From a static calibration of the condenser microphone it is estimated that, at the mouth of the loud-speaker horn, the sound amplitude per milliamp. loud-speaker current had the values 1/30, $\frac{1}{2}$, 1/8, $\frac{1}{4}$ dynes per sq. cm. for frequencies of 250, 500, 1000, 2000 v.p.s. respectively.

measurements by assuming constant efficiency is quite small *.

The electrodynamic loud-speaker thus appears to be generally satisfactory for reverberation work. In precision measurements in very reverberant rooms it would be necessary to allow for the variations indicated by the curves: the allowance has not been made in this paper.

II. Use in Reverberation Work.

The loud-speakers tested were used in reverberation work to determine the rate of decay of sound in a room. Briefly the method is to determine the duration of audibility in the room after the source is stopped, and then to repeat the experiment with a source of n times the activity. The difference observed is the time in which the sound in the room decays n fold. By conducting a whole series of tests it is possible to determine whether the decay factor for the room is the same for sounds of different initial intensity. This was done by Sabine † over a restricted range, up to about 4-fold, in his multiple organ pipe work. He found that the decay of sound of a given pitch in a room obeyed the logarithmic law,

$$\log \frac{I}{I_0} = At, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where I is the average intensity at the moment when the source is stopped and I_0 the average intensity at time t later, and A is a constant independent of the intensity of sound. Taking I_0 to be the minimum intensity necessary for audibility, and remembering that in the present case the original value of the average intensity is proportional to the square of the current through the loud-speaker, we may write

$$\log \frac{ki^2}{I_0} = At,$$

or

$$\log i = \tfrac{1}{2}At + \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where t is now the time required for the average intensity

* An error of 10 per cent. in an intensity ratio of 100^2 : 1 corresponds to a 1 per cent. change in the time taken for the reverberant sound in a room to decay in this ratio. For any but rooms of very long period this is of the order of the experimental error in the determination of audibility duration.

† Sabine, 'Collected Papers,' Paper No. 1, Harvard Univ. Press, 1922.

to fall to the minimum necessary for audibility or briefly the duration of audibility. There should thus be a linear relation between the loud-speaker current, plotted logarithmically, and the duration of audibility. From this the decay factor A for the room may be obtained.

Apparatus.

The arrangement of the loud-speaker and its source of alternating current was identical with that shown in fig. 1. A key was arranged which, when depressed, stopped the loud-speaker by breaking the high-tension circuit of the oscillator, and simultaneously started a time recorder. A second key was used in recording the instant at which the audibility was judged to cease in the chamber.

The loud-speaker was placed in the room under investigation, whilst the recording apparatus was situated outside. A position was chosen for the loud-speaker well away from all the walls and not directly facing any one, in order to minimise as far as possible any reaction effects. In one particular case the room appeared to have a resonance frequency very near—within, say, 1 vibration in about 2 seconds—to the frequency with which it was desired to work, and, owing to reaction upon the loud-speaker, considerable difficulty was experienced in tuning. Beats occurred which persisted for some time and then suddenly ceased. By slightly moving the loud-speaker the effect was suppressed, and the phenomenon did not recur at other frequencies tested.

The current was adjusted to a suitable high value, and ten readings were made of the duration of audibility. The sets of measurements were then repeated several times, using successively smaller values of the current. Finally the whole series was repeated in the reverse order, thus finishing up with the high current series with which the experiment was started. By this procedure the effect of any regular change in the efficiency of the loud-speaker due to change of temperature is eliminated. Several series of such readings were taken by two observers and in various positions in the room.

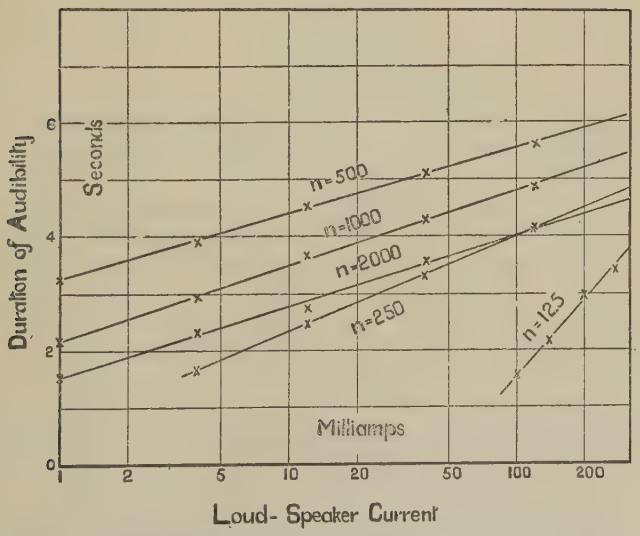
Results.

Measurements have been made in two different rooms. The first room had a volume of about 48,000 c.ft., a concrete

floor and ceiling, and brick walls with a large area of windows. It contained several pieces of machinery and some heaps of loose sand which made the exposed surfaces irregular in shape and miscellaneous in character. The electrodynamic loud-speaker was used in this building.

The work in the second room * was done much earlier with an electromagnetic type of loud-speaker, but the results are included here because of the greater simplicity of the structure of this room. It was quite empty and had a volume of about 9620 c.ft., a concrete floor, plaster ceiling, and brick walls with no windows. In neither case were the conditions very favourable for accurate reverberation work, since silence could not be obtained.

Fig. 4.



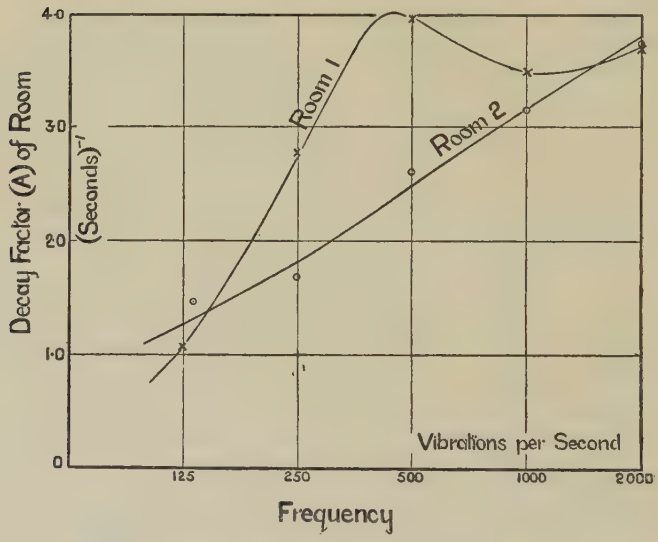
Relation between duration of audibility and loud-speaker current in room 1.

Fig. 4 shows the relation in room 1 between the logarithm of the loud-speaker current, and the duration of audibility

* We are indebted to the Director of the Building Research Board for permission to use this room.

for different values of the frequency. In most cases the current has been varied over a range of 120 fold, corresponding to a variation of the initial average intensity of over 14,000 fold. Over this wide intensity ratio the logarithmic relation, established by Sabine over a very restricted range, is still found to hold good.

Fig. 5.



Relation between decay factor of room and frequency.

The values of the constant A obtained from the curves of fig. 4 are shown plotted against the frequency in fig. 5, together with those obtained in room 2. While there appears to be no simple relation in the case of the first room, in the case of the second room, whose absorbing surfaces were not of such a miscellaneous character, a regular variation with the frequency was obtained.

V. *On the Calculation and Application of High Resistances of small Self-Inductance for all Frequencies.* By Raymond M. Wilmotte, *B.A.* (*of the National Physical Laboratory*) *.

Abstract.

In many accurate measurements it is necessary to know the exact phase-angle of high resistances of the order of several thousand ohms. In this case the capacity effects are often very large. In the paper, formulæ are given for the self-inductance of high resistances formed by long parallel wires of circular cross-sections and screened from earth by a cylindrical metal shield.

The formulæ for the use of such a standard as a ratio arm and potential divider are also given, together with its application in bridges.

I. Introduction.

THE use of high resistances in alternating-current measurements often leads to difficulties, owing to the residual self-inductance and the effect of capacity on the circuit. These effects become more pronounced as the frequency increases, and the effect of capacity, which is quite negligible for low resistances, usually becomes predominant when the resistance reaches values of several thousand ohms.

It has been usual to take as a standard of comparison of residual inductance a single long loop of wire with parallel sides, the formula for which was given by S. L. Brown †. It will be shown, however, that this formula only holds in practice if the middle point of the loop is at earth potential—a condition which does not usually obtain.

For high resistances a single loop of wire means a very cumbersome standard, and in this paper formulæ are obtained for a standard made of a large number of long parallel wires connected as shown in fig. 1, where the wires are not necessarily in the same plane. It is necessary, especially for high resistances, to screen the wires from the earth by means of a cylindrical metal shield.

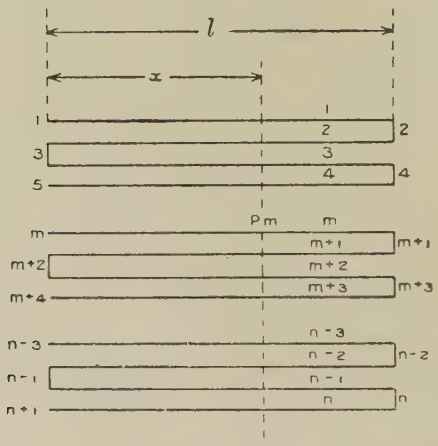
The adaptation to high voltages is complicated, since a very considerable length of wire is required from the

* Communicated by the Author.

† Phys. Rev. vol. xxix. p. 369 (1909).

necessity of keeping down the temperature rise. For these purposes voltages of the order of 2 to 10 per metre length of wire are commonly used, the current being 0·1 ampere or less. There is also the limitation imposed by the effect of the production of corona around the wire, due to the electric field between it and the shield. These considerations would require a number of systems of the type suggested to be put in series for high voltages. A phase displacement

Fig. 1.



would result, depending upon the capacity and voltage of the different shields to earth. This effect can, however, be calculated if the capacities of the shields to earth are known (either by measurement or by surrounding the whole with a large concentric screen connected to earth and calculating the capacities). In this connexion, when dealing with commercial frequencies, non-inductive resistances for high voltages can be constructed more satisfactorily by the method described by E. Orlich and H. Schultze *, which is more compact and allows of easier computation but is not suitable for higher frequencies.

Formulæ are also given for the use of the standard as ratio arms and as potential divider, and it is hoped that they may be found useful at audio frequencies and in developing bridge methods suitable for radio frequencies.

* *Archiv. f. Elek.* vol. i. p. 1 (1912),

II. Capacity Coefficients of n thin parallel Wires within a Cylinder.

The problem of the capacity between infinite parallel cylinders has not been completely solved, but an approximate solution can be found if the radii of the cylinders are small compared with their distances apart.

Consider n parallel thin conductors of radii $r_1, r_2, \ldots, r_n$ having polar coordinates (a_1, θ_1), (a_2, θ_2), $\ldots$, (a_n, θ_n) referred to the centre of the cylindrical metal screen of radius R as origin. The image of the wire A_r in the screen will be B_r, where $OB = R^2/a_r$.

Let $q_1, q_2, \ldots, q_n$ be the charges on the wires, the potentials of which are $v_1, v_2, \ldots, v_n$ respectively. We shall assume the dielectric constant to be unity.

Then, the potential of the screen will be given by

$$v_s = C - 2\sum_{r=1}^{r=n} q_r \log (a_r/R), \quad . \quad . \quad . \quad . \quad (1)$$

and the potential at the surface of the wire of radius r_m surrounding A_m is, if r_m is small, approximately given by

$$v_m = C + 2q_m \log \left(\frac{R^2 - a_m^2}{a_m r_m}\right) + 2\sum_{r=1}^{r=n} q_r \log \left(\frac{A_m B_r}{A_m A_r}\right), \quad . \quad (2)$$

in which the term having $r = m$ is left out in the last sum.

If the screen is connected to earth, we have

$$v_m = 2q_m \log \left(\frac{R^2 - a_m^2}{R r_m}\right) + 2\sum_{r=1}^{r=n} \log \left(\frac{a_r \,.\, A_m B_r}{R \,.\, A_m A_r}\right). \quad . \quad (3)$$

The potential coefficients are, therefore, given by

$$p_{m.m} = 2 \log \{(R^2 - a_m^2)/R r_m\} \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{and} \quad p_{m.r} = 2 \log \{(a_r \,.\, A_m B_r)/R \,.\, A_m A_r\}. \quad . \quad . \quad (5)$$

If R is large compared with a, so that a^2 can be neglected compared with R^2, these become

$$p_{m.m} = 2 \log (R/r_m) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\text{and} \quad p_{m.r} = 2 \log (R/A_m A_r). \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Since r is small compared with a, $p_{m.m}$ will usually be greater than $p_{m.r}$ unless R is infinite, when in the limit $p_{m.m} = p_{m.r}$.

The capacity coefficients are given by

$$k_{m.r} = \mathrm{D}_{m.r}/\Delta, \quad \ldots\ldots (8)$$

where

$$\Delta = \begin{vmatrix} p_{1.1}, & p_{2.1}, & \ldots., & p_{n.1}, \\ p_{1.2}, & p_{2.2}, & \ldots., & p_{n.2}, \\ \ldots & \ldots & \ldots & \ldots \\ p_{1.n}, & p_{2.n}, & \ldots., & p_{n.n}, \end{vmatrix} \quad \ldots\ldots (8)$$

and $\mathrm{D}_{m.r}$ is the minor of $p_{m.r}$ in this determinant.

Now these coefficients can be exactly represented by capacities $\mathrm{K}_{0.m}$ between any wire m and earth and $\mathrm{K}_{m.r}$ between any two wires m and r, where

$$\mathrm{K}_{0.m} = \sum_{r=1}^{r=n} k_{m.r} \quad \ldots\ldots\ldots (9)$$

and $$\mathrm{K}_{m.r} = -k_{m.r}. \quad \ldots\ldots\ldots (10)$$

Where there are a number of wires, the determinant of equation (8) becomes unmanageable except in special cases.

If $p_{m.r}$ is small compared with $p_{m.m}$ we have, neglecting small quantities of the second order,

$$k_{m.r} = -\frac{p_{m.r}}{p_{m.m} \cdot p_{r.r}} + \sum_{q=1}^{q=n} \left\{ \frac{p_{q.m}\, p_{q.r}}{p_{q.q}\, p_{m.m}\, p_{r.r}} \right\}, \quad \ldots (11)$$

in which $q \neq m$ or r and $p_{m.r}$ becomes negative, if $r = m$.

Now suppose all the wires to be distributed along the surface of a cylinder of radius a concentric with the shield and parallel to its axis. Let $\mathrm{R}/a = 1+\rho$, where ρ is small. Equations (4) and (5) become

$$p_{m.m} = 2 \log \left\{ \frac{\rho(2+\rho)a}{(1+\rho)r_m} \right\} \quad \ldots\ldots (12)$$

and

$$p_{m.r} = \log \left\{ 1 + \left[\frac{\rho(2+\rho)}{2(1+\rho)\sin \frac{1}{2}\theta_{m.r}} \right]^2 \right\}, \quad \ldots (13)$$

where

$$\theta_{m.r} = \theta_r - \theta_m.$$

Table I. gives the values of $p_{m.r}$ for various values of ρ and $\theta_{m.r}$, from which we can see when $p^2_{m.r}$ can be neglected compared with $p^2_{m.m}$, since the value of $p_{m.m}$ will usually be between 5 and 15 :—

TABLE I.

Values of $p_{m.r}$.

$\theta_{m.r}$ =	5°.	10°.	15°.	20°.	30°.	45°.	60°.	90°.	120°.	180°.
ρ=0·05	0·814	0·267	0·134	0·078	0·035	0·016	0·010	0·006	0·004	0·002
0·10	1·76	0·791	0·429	0·248	0·128	0·062	0·035	0·019	0·012	0·010
0·15	2·44	1·27	0·764	0·497	0·260	0·126	0·076	0·039	0·029	0·021
0·20	2·93	1·67	1·09	0·746	0·409	0·208	0·128	0·064	0·045	0·035
0·30	3·63	2·33	1·64	1·21	0·718	0·396	0·254	0·136	0·091	0·070
0·40	4·13	2·81	2·07	1·59	1·01	0·592	0·388	0·215	0·147	0·114
0·50	4·53	3·17	2·41	1·91	1·28	0·784	0·531	0·298	0·211	0·163

If ρ is small we can expand equation (13) and obtain

$$p_{m.r} = \frac{\rho^2}{\sin^2(\frac{1}{2}\theta_{m.r})}\left\{1-\rho+\frac{\rho^2}{2}\left(\frac{5}{2}-\frac{1}{\sin^2(\frac{1}{2}\theta_{m.r})}\right)+\dots\right\}.$$

Hence, neglecting small terms of the second order,

$$K_{m.r} = \frac{1}{p_{m.m}\,p_{r.r}}\left\{\frac{\rho^2(1-\rho)}{\sin^2(\frac{1}{2}\theta_{m.r})} - \rho^4\sum_{q=1}^{q=n}\left[\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})\sin^2(\frac{1}{2}\theta_{r.q})\,p_{q.q}}\right]+\dots\right\}, \quad (14)$$

in which $q \neq m \neq r$.

If all the wires are of the same radius r, so that

$$p_{m.m} = p_{r.r} = \dots \equiv p,$$

we have

$$K_{0.m} = \frac{1}{p}\left\{1+\frac{\rho^2(1-\rho)}{p}\sum_{q=1}^{q=n}\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})}\right\} \quad (15)$$

and

$$K_{m.r} = \frac{1}{p^2}\left\{\frac{\rho^2(1-\rho)}{\sin^2(\frac{1}{2}\theta_{m.r})} - \frac{\rho^4}{p}\sum_{q=1}^{q=n}\left[\frac{1}{\sin^2(\frac{1}{2}\theta_{m.q})\sin^2(\frac{1}{2}\theta_{r.q})}\right]\right\}, \quad (16)$$

in which as before $q \neq m \neq r$.

If $p_{m.r}$ is sufficiently small, the last term in equation (16) can be neglected. It should also be noticed that for this $K_{0.m}$ has the same value for all the wires.

III. STANDARD RESISTANCE.

(a) *General Theorem for* n *Impedances in Series.*

Consider n impedances Z_1, Z_2, ..., Z_n connecting the points 1 and 2, 2 and 3, ..., n and $(n+1)$ respectively.

The point 0 will be assumed to be at earth potential. Suppose the ends of these impedances be interconnected by capacities, the capacity connecting the points m and r being $C_{m.r}$. It is required to find the impedance of the whole, when the capacities are sufficiently small that their products can be neglected.

There will be two definitions of this impedance: one Z_0 will be the ratio of the potential difference across the whole network and the current entering at the point 1 excluding the earth-current to the network, and Z_1 will be the same but including the earth-current. In other words, the impedance will be Z_0 if the current is measured between the points 0 and 1, and Z_1 if the points 0 and 1 are on the same side of the point where the current is measured.

Let $i_1, i_2, \ldots, i_n$ be the currents and $V_1, V_2, \ldots, V_n$ be potentials across $Z_1, Z_2, \ldots, Z_n$ respectively. For shortness, we shall express the sum of these potential differences and impedances between the points m and r by $V_{m.r}$ and $Z_{m.r}$ respectively, so that

$$Z_{m.r+1} = \sum_{p=m}^{p=r} (Z_p) \quad \text{and} \quad V_{m.r+1} = \sum_{p=m}^{p=r} (V_p),$$

where $Z_{m.r}$ and $V_{m.r}$ are positive if $r > m$, and *vice versa*.

Now
$$V_m = Z_m \, . \, i_m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and
$$i_0 = i_m + \sum_{p=1}^{p=m} \sum_{q=0}^{q=n+1} (V_{p.q} C_{p.q}) \alpha \quad . \quad . \quad (18)$$

and
$$i = i_m + \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (V_{p.q} C_{p.q}) \alpha, \quad . \quad . \quad (19)$$

where i_0 and i are the currents entering the network, excluding and including respectively the earth-current, and $\alpha = \omega\sqrt{-1}$, the frequency being $\omega/2\pi$.

From these three equations, neglecting small quantities of the second order, we have

$$V_m/i_0 = Z_m - Z_m \sum_{p=1}^{p=m} \sum_{q=0}^{q=n+1} (Z_{p.q} C_{p.q}) \alpha \quad . \quad . \quad (20)$$

and
$$V_m/i = Z_m - Z_m \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (Z_{p.q} C_{p.q}) \alpha, \quad . \quad . \quad (21)$$

in which $Z_{p.q}$ is negative if $p > q$, and *vice versa*.

Since

$$\sum_{m=1}^{m=n}\left\{Z_m\sum_{p=1}^{p=m}\sum_{q=0}^{q=n+1}(Z_{p.q}C_{p.q})\alpha\right\}$$
$$=\sum_{p=1}^{p=n+1}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)\alpha-\sum_{m=1}^{m=n+1}(C_{0.m}Z_{0.m}Z_{m.n+1})\alpha,$$

the impedance of the network is given by

$$Z_0=\sum_{m=1}^{m=n}(V_m/i_0)$$
$$=Z_{1.n+1}-\left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)-\sum_{p=1}^{p=n}(C_{0.p}Z_{0.p}Z_{p.n+1})\right]\alpha$$

and . . . (22)

$$Z_1=Z_{1.n+1}-\left[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2)+\sum_{p=2}^{p=n+1}(C_{0.p}Z_{0.p}Z_{1.p})\right]\alpha,$$

. . . (23)

where $Z_0 i_0$ is the potential of the point 1 below earth, and

$$i_0=i\left[1-\sum_{q=1}^{q=n+1}(Z_{0.q}C_{0.q})\alpha\right]. \quad . \quad . \quad . \quad . \quad (24)$$

Also, if i' be the current leaving the network,

$$i'/i=1-\sum_{q=0}^{q=n+1}(Z_{0.q}C_{0.q})\alpha. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

(*b*) *Formulæ for Residual Inductance.*

Besides intercapacities, the wires have a small self-inductance L per unit length, given by Rosa *:

$$L=2[\log(2l/r)-1+\mu/4], \quad . \quad . \quad . \quad . \quad (26)$$

where l is the length of the wire, r its radius, μ the permeability of the wire, that of the dielectric being unity.

Also there are small mutual inductances M between the wires, given by *

$$M=\pm 2[\log(2l/d)-1+d/l], \quad . \quad . \quad . \quad . \quad (27)$$

where d is the distance apart of the wires. The mutual inductance between the wires p and q, connected in the same sequence as in fig. 1, will be negative if $(q-p)$ is odd

* "Self and Mutual Inductances of Linear Conductors," by E. B. Rosa, Bull. Bureau of Standards, vol. iv. p. 301 (1907).

and positive if $(q-p)$ is even. In general, the last term of equation (27) can be neglected.

It should be noticed that formulæ (4) and (5), (26) and (27) only hold for wires of circular cross-section.

Let us first assume that there are no capacities (which might be produced by terminals etc.) at the ends of the wires. Consider a point P_m on the wire m (fig. 1) distant x from m. Let Z_m, $M_{m.r}$, $K_{m.r}$, $K_{0.m}$ be the constants per unit length of this wire. Then

$$-\frac{di_{m+x}}{dx} = \sum_{r=0}^{r=n} (K_{m.r} V_{m+x.r+x})\,\alpha, \quad . \quad . \quad . \quad . \quad (28)$$

where i_{m+x} is the current at P_m and $V_{m+x.r+x}$ is the potential difference between P_m and P_r on the same level as P_m on the rth wire. Also

$$-\frac{dV_{m+x}}{dx} = i_{m+x} Z_m + \sum_{r=1}^{r=n} (M_{m.r} i_{r+x})\,\alpha. \quad . \quad . \quad (29)$$

Integrating equation (28) between the limits 0 and l, we have

$$i_m - i_{m+1} = \sum_{r=0}^{r=n} \left\{ K_{m.r} l i_1 \left[Z_{m.r} + (Z_r - Z_m)\frac{l}{2} \right] \alpha \right\},$$

where $Z_{m.r}$ is negative if $r<m$, and *vice versa*, i_m and i_{m+1} being the currents at the points m and $(m+1)$ respectively.

By taking the sum of this between 1 and $(m-1)$, we shall have an equation connecting i_m and i_1, by which i_m can be eliminated in the expression obtained on integrating equation (29). On rearranging, we finally have the impedances Y_0, Y_1 of the whole given by the general expressions :—

$$\begin{aligned} Y_0 &= \sum_{m=1}^{m=n} (V_m/i_0) \\ &= Z_{1.n+1} + \Bigg[\sum_{m=1}^{m=n} \sum_{r=1}^{r=n} (M_{m.r} l) - \sum_{m=1}^{m=n} \sum_{r=m+1}^{r=n} (K_{m.r} l A_{m.r}) \\ &\quad + \sum_{m=1}^{m=n} \left\{ K_{0.m} l \left[Z_{0.m} Z_{m+1.n+1} + Z_m l \left(\tfrac{1}{2} Z_{0.n+1} - \tfrac{1}{3} Z_m l \right) \right] \right\} \Bigg] \alpha, \end{aligned}$$

and . . . (30 A)

$$\begin{aligned} Y_1 &= Z_{1.n+1} + \Bigg[\sum_{m=1}^{m=n} \sum_{r=1}^{r=n} (M_{m.r} l) - \sum_{m=1}^{m=n} \sum_{r=m+1}^{r=n} (K_{m.r} l A_{m.r}) \\ &\quad - \sum_{m=1}^{m=n} \left\{ K_{0.m} l \left[Z_{0.m} Z_{1.m+1} - Z_m l \left(\tfrac{1}{2} Z_{0.1} - \tfrac{1}{3} Z_m l \right) \right] \right\} \Bigg] \alpha, \end{aligned}$$

. . . (30 B)

where

$$A_{m,r} = Z_{m+1,r+1}\left[Z_{m,r} + (Z_r - Z_m)\frac{l}{2}\right] + \frac{Z_{m,r}}{2}(Z_m - Z_r)l - (Z_m - Z_r)^2\frac{l^2}{6} \quad \text{if } (r-m) \text{ is even,}$$

and

$$A_{m,r} = Z_{m+1,r+1}\left[Z_{m,r} + (Z_r - Z_m)\frac{l}{2}\right] + \frac{Z_{m,r}}{2}(Z_m - Z_r)l - (Z_m - Z_r)\frac{l^2}{6} + \frac{1}{3}Z_m Z_r l^2 \quad \text{if } (r-m) \text{ is odd.}$$

Three special cases will be considered :—

(i.) If all the wires are equal and have a resistance R each, we have

$$Y_0 = nR + \left[L_{1,n+1} + 2\sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n} M_{m,r}l - \sum_{m=1}^{m=n}\sum_{r=m+1}^{r=n} R^2(K_{m,r}lA_{m,r}) + \sum_{m=1}^{m=n}\left\{K_{0,m}l\left[Z_{0,1}R(n-m+\tfrac{1}{2}) + R^2\left(\{n-m+1\}m - \frac{n}{2} - \frac{1}{3}\right)\right]\right\}\right]\alpha, \quad . \quad . \quad . \quad . \quad (31)$$

where $A_{m,r} = (r-m)^2 + \frac{1}{3}$ if $(r-m)$ is odd

and $A_{m,r} = (r-m)^2$ if $(r-m)$ is even.

In the equation for Y_1 the last term is

$$-\sum_{m=1}^{m=n}\left\{K_{0,m}l\left[Z_{0,1}R(m-\tfrac{1}{2}) + R^2(m^2 - m + \tfrac{1}{3})\right]\right\}\alpha.$$

(ii.) If the wires are all equally spaced, equation (31) can be written in the form :

$$Y_0 = nR + l\left[2\log\left\{\frac{(2l)^\gamma}{r^n}\right\} + 4\sum_{m=2}^{m=}\left\{(-1)^m(n-m+1)\left(\log d_{1,m} - \frac{d_{1,m}}{l}\right) + 2\left(\frac{n\mu}{4} - \gamma\right) - \sum_{m=1}^{m=n}\left\{(n-m+1)R^2K_{1,m}A_{1,m} - K_{0,m}\left[Z_{0,1}R(n-m+\tfrac{1}{2}) + R^2\left(\{n-m+1\}m - \frac{n}{2} - \frac{1}{3}\right)\right]\right\}\right]\alpha, \quad . \quad . \quad . \quad (32)$$

where $\gamma = 0$ if n is even (which is the usual case) and $\gamma = 1$

if n is odd ; $A_{1.m}$ has the same value as in equation (31) ; $d_{1.r}$ is the distance between the 1st and the rth wire. The last term in the equation for Y_1 is the same as in case (i.).

(iii.) If $K_{0.m}$ has the same value (K_0, say) for all the wires, equation (32) can be further simplified. This will occur if all the wires are evenly spaced round the circumference of a cylinder concentric with the shield, or, again, if ρ in equation (15) is sufficiently small—that is, the distance between the wires and the shield is small compared with its radius. In the latter case, however, there must be no bodies within the shield other than the wires used. Thus it would not necessarily hold if only a few of the wires were used and the rest connected to the shield or left floating.

With these conditions, equation (32) becomes

$$\begin{aligned} Y_0 = n\mathrm{R} + l\Big[& 2\log\left\{\frac{(2l)^\gamma}{r^n}\right\} \\ & + 4\sum_{m=2}^{m=n}\left\{(-1)^m(n-m+1)\left(\log d_{1.m} - \frac{d_{1.m}}{l}\right)\right\} \\ & + 2\left(\frac{n\mu}{4} - \gamma\right) - \mathrm{R}^2\sum_{m=2}^{m=n}\left\{(n-m+1)\mathrm{K}_{1.m}\mathrm{A}_{1.m}\right\} \\ & + \mathrm{K}_0\left(\mathrm{Z}_{0.1}\mathrm{R}\frac{n^2}{2} + \mathrm{R}^2\frac{n^3}{6}\right)\Big]\alpha. \quad . \quad . \quad . \quad . \quad (33) \end{aligned}$$

The last term in the equation for Y_1 is

$$-\mathrm{K}_0 l\left(\mathrm{Z}_{0.1}\mathrm{R}\frac{n^2}{2} + \mathrm{R}^2\frac{n^3}{3}\right)\alpha.$$

To allow for the capacities $C_{m.r}$ between the terminals at the points m and r and the earth-capacities $C_{0.m}$, $C_{0.r}$ between the terminals and earth, we can use equations (22) and (23), for the whole resistance can be considered to be made up of impedances of value (V_m/i) in series interconnected with capacities.

Hence. the total impedance is given by

$$Z_0 = Y_0 - \Big[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2) - \sum_{p=1}^{p=n}(C_{0.p}Z_{0.p}Z_{p.n+1})\Big]\alpha \quad . \quad (34)$$

and

$$Z_1 = Y_1 - \Big[\sum_{p=1}^{p=n}\sum_{q=p+1}^{q=n+1}(C_{p.q}Z_{p.q}^2) + \sum_{p=2}^{p=n+1}(C_{0.p}Z_{0.p}Z_{1.p})\Big]\alpha. \quad . \quad (35)$$

(c) *Application to Bridges.*

When a high impedance is put in a bridge a difficulty is met at once in defining the meaning of impedance, for, owing

to capacity currents, the current entering any specific part of the bridge may not equal the current leaving it. We shall consider as a typical case the simple four-arm bridge (fig. 2).

The condition for balance is

$$V_{AB}/V_{BC} = V_{DA}/V_{CD}.$$

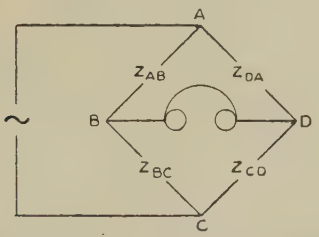
This can be written

$$(V_{AB} \cdot i_B)/(V_{BC} \cdot i_B) = (V_{DA} \cdot i_D)/(V_{CD} \cdot i_D)$$

or

$$Z_{AB}/Z_{BC} = Z_{DA}/Z_{CD}.$$

Fig. 2.



We see, therefore, that the impedance of any arm is defined as the ratio of the potential difference and the current at the end of the arm connected to the telephone.

Suppose the point c is earthed. The impedance will not include the earth capacity currents, so that we can use equation (22), in which $Z_{0.1} = Z_{BC}$ and B is taken as the point of the network to which the equation belongs. On the other hand, the impedance Z_{BC} will include the earth capacity currents, so that we must use equation (23) for it, putting $Z_{0.1} = -Z_{BC}$, where B is taken as the point 1.

If the telephone is earthed, we can consider that the earthing-wire is split in two on either side of B, so that the earth capacity current flows through B. The impedance of AB and BC is, therefore, given by equation (23), in which $Z_{0.1} = 0$ and B is taken as the point 1.

The last case of importance occurs when the telephone is kept at earth potential by means of a Wagner earth. In this case the earth capacity current does not flow through B and the impedance of AB and BC is given by equation (22), in which $Z_{0.1} = 0$ and B is taken as the point 1.

The same reasoning applies, of course, to the other two arms of the bridge CD and DA.

(d) *Case of a Single Loop.*

A special case of interest is that of two equal long parallel wires symmetrically situated with respect to the screen, with

terminals at the end having capacities $C_{1.2}$ between them and $C_{0.1}$ to the screen. If R_0 is the total resistance of the two wires together, we have from equation (34)

$$Z_0 = R_0 + \left\{ 4l[\log(2a/r) + \tfrac{1}{4}] - R_0^2 \frac{l}{3} K_{1.2} + R_0 l K_{0.1}\left(Z_{0.1} + \frac{R_0}{3}\right) + C_{0.1}(R_0 Z_{0.1} - C_{1.2} R_0^2) \right\} \alpha, \quad (36)$$

where r is the radius of the wires and $2a$ their distance apart. When the radius R of the screen is infinite, $K_{0.1} = C_{0.1} = 0$ and the equation becomes

$$Z_0 = R_0 + \left\{ 4l[\log(2a/r) + \tfrac{1}{4}] - \frac{R_0^2 l}{12 \log(2a/r)} - R_0^2 C_{1.2} \right\}, \quad (37)$$

which is the formula given by S. L. Brown *.

Let us consider how large the radius of the screen must be for this equation to hold.

If $Z_{0.1} = 0$—that is, one terminal is at earth potential—the last two terms in equation (35) become

$$-\frac{R_0^2 l}{6} \cdot \frac{\log\{(4\lambda^2+1)^2/\lambda/[4\lambda\mu(4\lambda^2-1)]\}}{\log\{\mu(4\lambda^2-1)/(4\lambda^2+1)\} \log\{\mu(16\lambda^4-1)/16\lambda^2\}} - R_0^2 C_{1.2}, \quad . \quad . \quad . \quad (38)$$

where $\lambda = R/d$ and $\mu = d/r$.

Also, if $Z_{0.1} = \frac{1}{2}R_0$—that is, the mid-point of the resistance is at earth potential—this becomes

$$-\frac{R_0^2 l}{12} \cdot \frac{1}{\log\{\mu(4\lambda^2-1)/(4l^2+1)\}} - R_0^2(C_{1.2} + \tfrac{1}{2}C_{0.1}). \quad (39)$$

When λ is large, expression (39) is very nearly identical with the expression for an infinitely distant screen for the measured capacity between the terminals is $(C_{1.2} + \frac{1}{2}C_{0.1})$. The same is not true for expression (38).

TABLE II.

Coefficient of $R_0^2 l$ in expression (36), $Z_{0.1} = 0$.

λ =	10	100	1000	10,000	
μ = 10	0	−0·0144	−0·020	−0·024	−0·036
= 100	0·0045	0	−0·0046	−0·0072	−0·018
=1000	0·0096	0·0034	0	−0 0022	−0·012

In Table II. the value of the coefficient of $R_0^2 l$ of the first term of that expression is given for various values

* *L. c. ante.*

of λ and μ. It will be seen that, as μ will usually lie between 100 and 1000, this coefficient will require an enormous value of λ to approach its limiting value. Thus, if $\mu = 100$ and $d = 1$ cm., this coefficient only reaches half its limiting value when all objects connected to earth are removed to a distance of one kilometre.

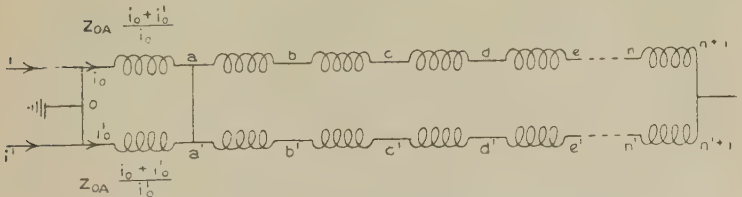
A similar result is obtained when Z_1 of equation (35) is taken instead of Z_0. Hence S. L. Brown's formula only applies when the mid-point of the resistance is at earth potential; but we saw in section III C. that in bridges $Z_{0.1}$ was either zero or positive, so that the conditions necessary for S. L. Brown's formula do not obtain. Experimental agreement was obtained because only differences were being measured, and the effect of the closeness of the earth would be substantially the same in both cases.

IV. Standard Ratio Arms.

(a) *General Theorem for Two Impedances in parallel.*

Consider n impedances in parallel with n' impedances (n does not necessarily equal n') interconnected by capacities at all points between the impedances. Let Z_{0A} be the impedance between the point a and a' and 0, which is connected to earth. This impedance can be split up into two impedances in parallel, $Z_{0A}(i_0 + i'_0)/i_0$ and $Z_{0.A}(i_0 + i'_0)/i'_0$, carrying the currents i_0 and i'_0 respectively. (Fig. 3.)

Fig. 3.



Using the same notation as previously, we have

$$V_m = Z_m i_m,$$

and

$$i_0 = i_m + \sum_{p=a}^{p=m} \sum_{q=0}^{q=n+1} (C_{p.q} V_{p.q}) \alpha + \sum_{p=a}^{p=m} \sum_{q=a'}^{q=n'+1} (C_{p.q} V_{p.q}) \alpha \quad (40)$$

and

$$i = i_m + \sum_{p=0}^{p=m} \sum_{q=0}^{q=n+1} (C_{p.q} V_{p.q}) \alpha + \sum_{p=a}^{p=m} \sum_{q=a'}^{q=n'+1} (C_{p.q} V_{p.q}) \alpha, \quad (41)$$

and similarly for i'_0 and i'.

Now,

$$\sum_{m=0}^{m=n}(V_m) = \sum_{m=0}^{m=n'}(V_m).$$

Writing P_0 and P'_0 for the expressions of the impedances as given in section III. for each of the two networks in parallel (these experiments will, of course, not contain the terms involving the capacities or mutual inductances between one network and the other), we have

$$\frac{i_0}{i'_0} \equiv \frac{Z'_0}{Z_0} = \sigma\left\{1+\left[\frac{P'_0}{Z_{a'.n'+1}} - \frac{P_0}{Z_{a.n+1}} + \sum_{p=a}^{p=n+1}\sum_{q=a'}^{q=n'+1} C_{p,q}(Z_{p.n+1}+Z_{q.n'+1})\left(\frac{Z_{a'.q}}{Z_{a'.n'+1}} - \frac{Z_{a.p}}{Z_{a.n+1}}\right)\right]\alpha\right\}, \quad . \quad . \quad . \quad (42)$$

where $\sigma = Z_{a'.n'+1}/Z_{a.n+1}$ and Z_0, Z'_0 are the effective impedances of each of the two networks in parallel. P_0 and P_0' are given by equation (22), where $Z_{0.a} = Z_{0.A}\left(1+\frac{1}{\sigma}\right)$ and $Z_{0.a'} = Z_{0.A}(1+\sigma)$.

Also

$$\frac{i}{i'} \equiv \frac{Z_1'}{Z_1} = \sigma\left\{1+\left[\frac{P_1'}{Z_{a'.n'+1}} - \frac{P_1}{Z_{a.n+1}} + \sum_{p=a}^{p=n+1}\sum_{q=a'}^{q=n'+1} C_{p.q}(Z_{p.n+1}+Z_{q.n'+1})\left(\frac{Z_{a'.q}}{Z_{a'.n'+1}} - \frac{Z_{a.p}}{Z_{a.n+1}}\right)\right]\alpha\right\}, \quad . \quad . \quad . \quad (43)$$

where P_1 and P_1' are given by equation (23).

P_0, P_0', Z_0, Z_0' of equation (42) are the same as P_1, P_1', Z_1, Z_1' of equation (43), except that the former refer the impedances to the current entering the network including the earth capacity current, while the latter refer to the current entering the network excluding the earth capacity current.

(b) *Formulæ for Ratio.*

We shall now apply the last result to the calculation of the true ratio of the standard used as ratio arms.

As before, we shall assume at first that there are no capacities at the ends of the wires. Consider a point P_m on the wire m (fig. 1) distant x from m. With the same notation as before, we have

$$-\frac{di_{m+x}}{dx} = \sum_{r=0}^{r=n}(K_{m.r}V_{m+x.r+x})\alpha + \sum_{r=a'}^{r=n'}(K_{m.r}V_{m+x.r+x})\alpha \quad . \quad (44)$$

and

$$-\frac{dV_{m+x}}{dx} = i_{m+x}Z_m + \sum_{r=a}^{r=n}(M_{m.r}i_{r+x})\alpha + \sum_{r=a'}^{r=n'}(M_{m.r}i_{r+x})\alpha, \quad (45)$$

where $M_{m.r}$ is given by equation (27). It should be noticed that, if the current enters the two arms at the same end, the mutual inductance between one wire m in one arm and one wire r in the other is negative if $(r-m)$ is odd and positive if $(r-m)$ is even.

To make the conditions more general, we shall assume the arms to be connected in series with external impedances Z_{Aa} and $Z_{Aa'}$, the standard containing n and n' wires respectively numbered from a to n and a' to n'.

These external impedances will be assumed to have zero mutual inductance with the standard, and there will, of course, be no capacity between them and the standard, since the latter is completely screened.

From equations (44) and (45), by integrating between the limits 0 and l and neglecting small terms of the second order, we obtain a general expression for $(Z_{A.n'+1}/Z_{A.n+1})$. The complete expression is lengthy, and, as the only case of importance is that when all the wires are equal and of resistance R, the simplified results in these conditions are given by

$$\frac{Z_{A.n'+1}}{Z_{A.n+1}} = \frac{Z_{A.a'}+Q'}{Z_{A.a}+Q}\left[1+R^2\sum_{p=a}^{p=n}\sum_{q=a'}^{q=n'}\left\{K_{p.q}\,l\left(\frac{B'_{p.q}}{Z_{A.a'}+Q'}-\frac{B_{p.q}}{Z_{A.a}+Q}\right)\alpha\right\}\right.$$
$$\left.+\left(\frac{1}{Z_{A.a'}+Q'}-\frac{1}{Z_{A.a}+Q}\right)\sum_{p=a}^{p=n}\sum_{q=a'}^{q=n'}(M_{p.q}\alpha)\right], \quad . \quad . \quad (46)$$

where Q and Q′ are the expressions of the impedances as given in equations (31), (32), and (33) for each of the two radio arms of the standard, and

$$B'_{p.q} = (n'-q)(q-\tfrac{1}{2})+q-\tfrac{1}{2} \text{ if } q-p \text{ is odd},$$
$$= (n'-q)(q-\tfrac{1}{2})+q-\tfrac{2}{3} \text{ if } q-p \text{ is even},$$

and
$$B_{p.q} = (n-p)(p-\tfrac{1}{2})+p-\tfrac{1}{2} \text{ if } q-p \text{ is odd},$$
$$= (n-p)(p-\tfrac{1}{2})+p-\tfrac{2}{3} \text{ if } q-p \text{ is even}.$$

To allow for the capacities between the terminals at the ends of the wires, we can now use equations (42) and (43), in which we substitute $(Z_{A.n'+1}/Z_{A.n+1})$ as given in equation (46) for σ.

(c) *Application to Bridges.*

The same arguments can be applied regarding the application of ratio arms in bridges as was used when a non-inductive resistance was considered. Let AB and AD

(fig. 2) be the ratio arms. Four cases arise :

(1) When C is earthed, the impedances Z_{AB} and Z_{AD} will not include the earth capacity currents, so that equation (42) will apply. The points B and D (which are electrically the same when balance is obtained) will correspond to the point a of the ratio arms and $Z_{0a}=Z_{BC}$ and $Z_{0a'}=Z_{DC}$.

(2) When A is earthed, the earth capacity currents will be included in the impedances Z_{AB} and Z_{AD}, so that equation (43) will now hold. The points B and D will, as before, correspond to the point a of the ratio arms, and we must put $Z_{0.a}=-Z_{AB}$ and $Z_{0.a'}=-Z_{AD}$.

(3) When the telephone is earthed at B or D, the earth capacity currents will be included and equation (43) must be used. The points B and D will correspond to the point a of the ratio arms and $Z_{0.a}=Z_{0.a'}=0$.

(4) When the telephone is kept at earth potential by a Wagner earth, equation (42) will hold. The points B and D will correspond to the point a of the ratio arms and $Z_{0.a}=Z_{0.a'}=0$.

V. Standard Potential Divider.

(a) *General Formulæ.*

In this case we require to find the ratio of the voltage between any two points r and s and the total voltage across the resistance. It will be supposed that no current is taken at the points r and s, but the capacity of the leads etc. connected to those two points must be taken into account in the usual way.

From equation (20) we have

$$\frac{V_{r.s}}{i_0}=\sum_{m=r}^{m=s-1}(V_m/i_0)$$
$$=Z_{r.s}\Big[Z_{r.s}\sum_{p=1}^{p=r}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q})+\sum_{p=r+1}^{p=s-1}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.s})\Big]\alpha, \quad . \ . \ . \quad (47)$$

giving the potential difference between the points r and s when the potential divider is assumed to be made up of n impedances in series.

By putting $r=1$ and $s=n+1$, we obtain the potential difference across the whole. From this, we have

$$\frac{V_{r.s}}{V_{1.n+1}}=\frac{Z_{r.s}}{Z_{1.n+1}}\left\{1-\left[\sum_{p=2}^{p=r}\sum_{q=0}^{q=n+1}(C_{p.q}+Z_{p.q})\right.\right.$$

$$+\frac{1}{Z_{r.s}}\sum_{p=r+1}^{p=s-1}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.s})$$

$$\left.\left.-\frac{1}{Z_{1.n+1}}\sum_{p=2}^{p=n}\sum_{q=0}^{q=n+1}(C_{p.q}Z_{p.q}Z_{p.n+1})\right]\alpha\right\}. \quad (48)$$

Now suppose the tapping points are at points distant x and y from r and s respectively. Let us call these points $(r+x)$ and $(s+y)$.

From equations (28) and (29) it can be shown that

$$\frac{V_{r+x.s+y}}{i_1}=Z_{r+x.s+y}+\left[\sum_{p=1}^{p=n}\left\{M_{s.p}y-M_{r.p}x+\sum_{q=r}^{q=s-1}(M_{p.q}l)\right\}\right.$$

$$-\sum_{p=r-1}^{p=s-1}\sum_{q=p+1}^{q=n}(K_{p.q}lA_{p.q})$$

$$-\sum_{p=1}^{p=r-1}K_{0.p}l\left\{Z_{0.p}Z_{p+1.r}+Z_pl\left(\frac{1}{2}Z_{0.r}-Z_p\frac{l}{3}\right)\right\}$$

$$-Z_rx\sum_{p=0}^{p=n}(\tfrac{1}{2}K_{rp}xB_{r.p})$$

$$+\sum_{p=1}^{p=s-1}K_{0.p}l\left\{Z_{0.p}Z_{p+1.s}+Z_pl\left(\frac{1}{2}Z_{0.s}-Z_p\frac{l}{3}\right)\right\}$$

$$\left.+Z_sy\sum_{p=0}^{p=n}(\tfrac{1}{2}K_{s.p}yB_{s.p})\right],$$

where . . . (49)

$$A_{p.q}=\left[Z_{p.q}+(Z_q-Z_p)\frac{l}{2}\right]Z_{p+1.q+1}+\tfrac{1}{2}Z_{p.q}(Z_p-Z_q)l$$

$$-\frac{l^2}{6}(Z_p-Z_q)^2 \quad \text{if } (q-p) \text{ is even,}$$

and

$$A_{p.q}=\left[Z_{p.q}+(Z_q-Z_p)\frac{l}{2}\right]Z_{p+1.q+1}+\tfrac{1}{2}Z_{p.q}(Z_p-Z_q)l$$

$$-\frac{l^2}{6}(Z_p+Z_q)^2+Z_pZ_ql^2 \quad \text{if } (q-p) \text{ is odd.}$$

Also

$$B_{r.p}=Z_{r.p}+(Z_p-Z_r)\frac{x}{3} \quad \text{if } (p-r) \text{ is even,}$$

and

$$B_{r.p}=Z_{r.p+1}-(Z_p+Z_r)\frac{x}{3} \quad \text{if } (p-r) \text{ is odd.}$$

(For $B_{s.p}$ put y instead of x and s instead of r.)

The general expression for $(V_{1.n+1}/i_1)$ is given by equation (30 B). By dividing equation (49) by this, we obtain the ratio $(V_{r+x.s+y}/V_{1.n+1})$.

To allow for the capacities of the terminals, this ratio must be substituted for $(Z_{r.s}/Z_{1.n+1})$ in equation (48).

This may appear very laborious, but at the worst when there are many wires it only involves very simple arithmetic. The expression $(V_{r+x.s+y}/i_1)$ is usually simplified by the fact that all the wires will in general be of the same resistance R, and very often the earth capacity terms will be large compared with the other capacity terms. Besides this, in the usual case, $r=1$ and $x=y=0$.

When all the wires are of resistance R, the values of $A_{p.q}$ and $B_{p.q}$ simplify to

$$A_{p.q} = [(q-p)^2+\tfrac{1}{3}]R^2 \quad \text{if } (p-q) \text{ is odd,}$$

and

$$A_{p.q} = (q-p)^2R^2 \quad \text{if } (p-q) \text{ is even.}$$

Also

$$B_{r.p} = \left(p-r+\frac{x}{3}\right)R \quad \text{if } (p-r) \text{ is odd,}$$

and

$$B_{r.p} = (p-r)\,R \quad \text{if } (p-r) \text{ is even.}$$

(b) *Application.*

Apart from the general use of the potential divider at audio and radio frequencies, the standard may be of special use for obtaining small known voltages at radio frequencies, the voltage across the whole resistance being measured by an electrostatic voltmeter. When very low voltages are required, it would be easier to connect a low variable resistance in series with the standard and take off the desired voltage across that resistance. It is, of course, assumed that the frequency is never so high that terms containing squares of the capacities cannot be neglected.

We have seen that, to obtain a calculable solution, it was necessary to have the shield fairly close to the wires. When dealing with very high voltages, this may bring a difficulty

of corona effects and sparking directly to the screen. If a number of standards are used in series this might largely be obviated by connecting the screen to one of its terminals, so that the potential difference in any one of them is only a fraction of the total. It will then become necessary to measure or calculate the capacity of the various screens to earth. For calculation, the simplest case would be to place all the standards in a line and surround the whole with a concentric metal shield (which can be a simple wire mesh), when capacity of each standard to earth will be

$$\frac{l}{2\log(r_1/r_2)},$$

where r_1 and r_2 are the radii of the external screen and of the standard respectively, l being the length.

VI. General Construction.

(a) *Design.*

The case of a 10,000 ohm standard will be considered. If No. 47 manganin wire, radius 0·0025 cm., is used, it may consist of 40 wires about 106 cm. long. The angle subtended at the centre by two consecutive wires will thus be 9°. From Table I. it must therefore be of the order of 0·1 or less. Suitable values are :

Internal radius of screen . . = 2 inches.
Distance of wires from centre = 1·8 ,,

Hence

$$\rho = 0{\cdot}111.$$

If there are no lumped capacities at the terminals, the total impedances of the 40 wires in series will be, from equation (33),

$$Y_0 = 10{,}000 + {\cdot}00935\alpha$$

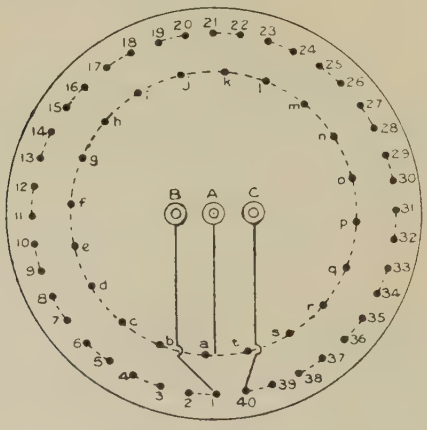
and

$$Y_1 = 10{,}000 - {\cdot}0201\alpha.$$

To allow this standard to be used for a number of values of resistance, the wires must be connected to terminals at one end ; at the other end they would simply be held taut by springs, to which they would not be electrically connected. In order to keep the wires in position along their whole length, they could be supported at intervals by ebonite bridges.

A suitable arrangement of the terminals is shown in fig. 4. The large dots represent the terminals (which may take the form of a split wire) to which the wires are fixed. The resistance wires 1 and 2, 3 and 4, etc., are connected at the further end, and the wires 2 and 3, 4 and 5, etc., can be connected by thin copper wires at the terminals. The other circle of terminals are all connected together by a thin copper wire and serves as a connecting-link between the last wire and terminal A.

Fig. 4.



Thus, if terminal 10 is connected to *e*, the resistance will be 2500 ohms. All the other wires will be connected together and to earth. In such a case the values of the capacities to earth will be slightly altered, because of the other earthed wires and terminals. The capacity to earth of any wire will be its usual value plus the sum of the capacities between the wire under consideration and all the earthed wires.

The correction due to the return path $a, b, c, d, e, \ldots$ can be allowed for, if the capacities are known and the mutual inductance is negligible.

Three terminals ABC are shown to allow for the standard to be used as ratio arms, one arm starting at wire 1 and the other at wire 40. In this case it would be advisable to cut the return wire $a, b, c \ldots$ at some point in between the two arms.

The measurement of the terminal capacities will be somewhat lengthy, owing to their large number. Fortunately, the work is considerably shortened owing to the symmetry

of the arrangement. It is necessary to know the capacity of any terminal to the screen, to any other terminal, and to the return wire.

Connect all the wires except the mth and rth together. Call this A and the screen S. By connecting m, r, S, and A in various ways we can find their capacity thus.

Connecting A and r to S and finding the capacity to m, we have

$$C_{Am} + C_{mr} + C_{mS} = C_1.$$

Connecting r to S and A to m and finding the capacity between them, we have

$$C_{Ar} + C_{AS} + C_{mS} + C_{mr} = C_2.$$

Connecting m and r to S and finding the capacity to A, we have

$$C_{AS} + C_{Am} + C_{Ar} = C_3.$$

Connecting A to S and m to r and finding the capacity between them, we have

$$C_{m.S} + C_{r.S} + C_{A.m} + C_{A.r} = C_4.$$

Therefore, since m and r are symmetrical,

$$\begin{aligned} C_{A.r} = C_{A.m} &= \tfrac{1}{2}(C_1 + C_3 - C_2), \\ C_{A.S} &= C_2 - C_1, \\ C_{r.S} = C_{m.S} &= \tfrac{1}{2}(C_4 + C_2 - C_1 - C_3), \\ C_{m.r} &= C_1 - \tfrac{1}{2}C_4. \end{aligned}$$

The value of C_1 must be found for all values of r. From this, since C_4 is from symmetry independent of r, we can find the values of $C_{m.r}$ for all values of r, and, since

$$C_{m.S} = C_{0.m} + \sum_{p=1}^{p=n} (C_{m.p}) - C_{m.r},$$

where $C_{0.m}$ is the capacity to the screen alone, we can find $C_{0.m}$.

The intercapacities and capacities to earth of the terminals A, B, and C will have to be found in a similar way.

It will be seen that the capacities of the wires can be measured instead of calculated, when the wires are not permanently connected together. When this is done, the limitation of having to screen close to the wire vanishes.

(b) *Accuracy.*

The intercapacities of the terminal can be measured by the method of L. Hartshorn *, by which these small capacities

* Proc. Phys. Soc. vol. xxxvi. p. 399 (1924).

can be measured to within $0{\cdot}02\mu\mu$F. The error in the residual inductance due to this will, in a 10,000 ohm standard, be of the order of 005α.

The main term of the residual inductance is due to the earth capacities $K_{0,m}$, the other terms being but a few per cent. of this one. If errors of 10 per cent. occur in measuring the radius of the wires and the distance of the wires from the shield, the error in $K_{0,m}$ will be, for the case under consideration, of the order of 10 per cent. for the worst case, when all the errors are cumulative. Hence the maximum possible error in calculating the residual inductance of the standard, taking the error due to assumption of the wire being infinitely long into account, is about 11 per cent.

The accuracy of calculation depends largely on the accuracy of the measurement of the radius of the wire and of the distance between the wire and the shield, each representing a possible error of about 5 per cent. in the residual inductance for the case considered. To reduce the quadrature component, it would be necessary to use a larger shield and obtain $K_{0,m}$, $K_{m,r}$ by measurement

January 13, 1926.

VI. *Atomic Structure and the Magnetic Properties of Coordination Compounds.* *By* L. C. Jackson, *M.Sc., Ph.D., A.Inst.P., "1851 Exhibition" Senior Student* *.

THE magnetic properties of the coordination compounds of the elements between chromium and copper and their possible interpretation in terms of atomic structure have been discussed by a number of writers recently. Most of the authors take as their basis the scheme for the distribution of the electrons among the sub-groups of the various atomic levels put forward independently by Stoner † and Main-Smith ‡ for the case of normal atoms and the ions of simple salts. The proposed distributions of the electrons in and around the coordinating atoms differ, however, considerably in detail, and it is proposed here to discuss the various schemes put forward and to endeavour to show which is the most probable.

Our knowledge of the magnetic properties of coordination compounds is derived from the determinations of Oxley §,

* Communicated by the Author.
† Phil. Mag. xlviii. p. 714 (1924).
‡ 'Chemistry and Atomic Structure,' London, 1924.
§ Proc. Camb. Phil. Soc. xvi. p. 102 (1910-12).

Rosenbohm *, and Welo †. Oxley has shown that potassium ferrocyanide is diamagnetic but that potassium ferricyanide is paramagnetic, the ferric atom possessing approximately ten Weiss magnetons. In these cases the properties of the metallic atom are very different from those possessed by that particular atom in simple salts.

Rosenbohm ‡ has determined the properties of a large number of complex ammines of chromium, cobalt, nickel and copper, together with those of platinum, iridium, ruthenium, and rhodium. We will confine ourselves here to the first group of compounds. Rosenbohm found that the sixfold compounds of chromium (Cr^{+++}) and nickel (Ni^{++}) were paramagnetic and possessed the same number of magnetons as these elements do in their simple salts, *i. e.*, approximately 19 and 16 respectively. A fourfold compound of nickel was also found to be paramagnetic, but to contain approximately 13 magnetons. The fourfold compounds of copper (Cu^{++}) were shown to be paramagnetic, with a magneton number somewhat smaller than that of the cupric ion in simple salts. The compounds of cobalt were found to be diamagnetic.

Rosenbohm's data, as Cabrera § has observed, require correction, firstly, because he made use of the value $-0{\cdot}75 \times 10^{-6}$ for the susceptibility of water instead of the now accepted value $-0{\cdot}719 \times 10^{-6}$, and secondly, because he did not apply any correction for the diamagnetic properties of the atoms or groups surrounding the central coordinating atom. These corrections are both relatively small and are of opposite sign, so that the corrected values do not differ greatly from Rosenbohm's original figures. Any of his data quoted in this paper have been corrected as mentioned above.

Welo ‖ has recently determined the magnetic properties of a number of complex ferro- and ferricyanides. He found that, with one doubtful exception ¶, all the ferrocyanides

* *Zeit. für Phys. Chem.* xciii. p. 693 (1919).

† 'Nature,' cxvi. p. 359 (1925).

‡ The magnetic properties of a few of the coordination compounds have also been measured by Mlle. Feytis (*C. R.* clii. p. 708 (1911)). In some cases the results agree with those of Rosenbohm, but in others there are considerable discrepancies. Rosenbohm believes, in all probability correctly, that his data are the more trustworthy on account of the very special care he took to obtain absolutely pure compounds and to ensure the reproducibility of the results.

§ *J. de Phys. et le Radium*, iii. p. 443 (1922).

‖ *Loc. cit.*

¶ See Welo and Baudisch, 'Nature,' cxvi. p. 606 (1925).

were diamagnetic. The ferricyanides were, however, paramagnetic and all contained approximately 10 magnetons.

These experimental results have been discussed recently by Welo and Baudisch *, Bose †, and Cabrera ‡.

Starting from Sidgwick's § ideas as to the number of electrons transferred to or shared with the central coordinating atom, Welo and Baudisch calculate the total number of electrons associated with the central atom ||. They thus obtain the following numbers for the elements mentioned (= atomic number + net number of electrons transferred or shared), $Cr^{+++}=33$, $Fe^{+++}=35$, $Fe^{++}=36$, $Co^{+++}=36$, Ni^{++} (sixfold) $=38$, (fourfold) $=34$, $Cu^{++}=35$.

The value 36 corresponds to the atomic number of argon, the next higher rare gas. The structure of the central atom when the "effective atomic number" is equal to 36 is then taken to be similar of that of argon It would thus be expected that these compounds would be diamagnetic, as is actually the case.

Those compounds for which the "effective atomic number" is not equal to 36 are paramagnetic. Welo and Baudisch, in these cases, distribute the electrons among the various possible atomic levels in such a way as to lead to the observed magneton numbers. For the case of Fe^{+++}, in which 9 additional electrons are to be disposed of, they assign 5 of the 9 to the N level making it complete with 8 (actually only the N_{11}, N_{21}, and N_{22} sub-groups have then been completed), and assign the remaining 4 to the M level. There are then 17 electrons in this level, as there are in this level for the divalent copper ion. Since this ion possesses about 10 Weiss magnetons, the authors say that it is therefore to be expected that the ferricyanides would possess the same number. This is actually the case.

By assigning 5 of the available electrons to the N level of the chromium atom in the complex salts and 4 to the M level, this atom is made to simulate the structure of the divalent cobalt ion in its simple salts. Experimentally divalent cobalt gives a magneton number of about 24–25, which does not agree with the value 19 found in the complex chromium compounds. Welo and Baudisch, however, state that cobalt is anomalous and quote Sommerfeld's 1923

* *Loc. cit.*

† *Zeit. für Phys.* xxxv. p. 219 (1925); 'Nature,' cxvii. p. 84 (1926).

‡ *J. de Phys. et le Radium*, vi. p. 276 (1925).

§ Trans. Chem. Soc. cxxiii. p. 725 (1923).

|| We shall confine the discussion here to those compounds with only one central metallic atom.

paper * as showing that a value 19·2 is expected for this ion. This argument does not seem very convincing, especially as the paper quoted has been superseded by later work †, and the divalent cobalt ion can hardly be considered as being in an '*s*' state.

For the sixfold nickel compounds, for which there are 10 disposable electrons, the central nucleus is supposed to be similar to the strontium atom with atomic number 38. This is presumed to contain 2 Bohr magnetons or 14·1 Weiss magnetons. Again the agreement is not striking.

With the fourfold copper compounds, 6 electrons are to be added. These are supposed to complete the N level (actually the first three sub-groups) leaving the M level as in the simple divalent copper ion, and hence the Weiss magneton number also the same. Actually the magneton number for the coordination compounds of Cu^{++} is somewhat less than that of the Cu^{++} ion in simple salts, 9 instead of about 9·7.

Welo and Baudisch's treatment of the paramagnetic coordination compounds is thus not particularly successful, and it may be noted that a satisfactory account of the magnetic properties of atoms cannot be given without considering the distribution of the electrons among the sub-groups of the various levels. Atoms or ions containing the same total number of electrons in the various levels may have different magnetic properties if the distributions among the sub-groups of the levels are different.

The objection may be raised to the scheme proposed by Welo and Baudisch that it does not bring out the character of the combination. The electron distribution does not show any evidence of the coordination numbers 6 or 4. The same objection may be made to the scheme proposed by Bose now to be discussed. An arrangement of the outer electrons corresponding to the known facts of the structure of these compounds has been proposed and discussed by Fowler ‡. It will be shown later how the magnetic properties can be interpreted in terms of these ideas.

Bose in his treatment of the problem also defines the "effective atomic number" in a way which, though different in principle, arrives at the same results as that of Sidgwick. He then distributes the electrons among the various possible atomic levels in a way rather similar to that of Welo and Baudisch. He then states that the magneton number of

* *Zeit. f. Phys.* xix. p. 226 (1923).
† *Atombau u. Spektrallinien*, 4te Auflage, p. 630.
‡ Trans. Farad. Soc. xix. p. 102 (1923).

any of these coordination compounds, expressed in Bohr magnetons, can be calculated from the following formula :— $Z-Z'=n$, in which Z=atomic number of next rare gas, in this case $A=36$, $Z'=$"effective atomic number" of central coordinating atom, n=number of Bohr magnetons. The numbers so obtained are as follows :—$Cr^{+++}=3$, $Fe^{+++}=1$, $Fe^{++}=0$, $Co^{+++}=0$, Ni^{++} (sixfold) $=2$, Ni^{++} (fourfold) $=2$, $Cu^{++}=1$.

The electron distributions proposed by Bose are given in Table I.

TABLE I.

Ion.	Kind of compound.	No. of electrons.							Total no. of electrons.		Difference.	Coord. no.
		M		N			O					
		32	33	11	21	22	11	21	imple ion.	Coord. atom.		
Cr^{+++}	simple ...		3						21		12	6
	complex...	4	3	2	2	4				33		
Fe^{+++}	simple ...		4	1					23		12	6
	complex...	4	6	1	2	4				35		
Fe^{++}	simple ...		4	2					24		12	6
	complex ..	4	6	2	2	4				36		
Co^{+++}	simple ...	2	4						24		12	6
	complex...	4	6	2	2	4				36		
Ni^{++}	simple ...	2	6						26			
	complex...	2	6	2	2	4				34	8	4
	complex...	2	6	2	2	4	2	2		38	12	6
Cu^{++}	simple ...	2	6	1					27		8	4
	complex...	4	6	1	2	4				35		

Such a rule as $Z-Z'=n$ does not seem likely to possess any definite physical meaning, containing as it does a number Z, which the coordinating atom may be said to strive to attain. In another paper * dealing with the distribution of the electrons among the M_{32} and M_{33} sub-groups for the normal atoms, and the ions of the simple salts of the elements of the first transition group, Bose has proposed the rule $M_{33}+N_{11}-M_{32}=n$, in which M_{33} etc. represent the number of electrons in the sub-group and n=number of Bohr magnetons. When, however, the sub-group is completed, the number of electrons in it count as zero, since it is generally accepted that the magnetic moment of a completed sub-group is zero. It would seem that an extension of this rule to the case of the coordination compounds would be physically more probable than the rule, $Z-Z'=n$, actually proposed.

It is easily seen that the obvious extension of the rule

$$M_{33}+N_{11}+N_{22}+O_{11}-M_{32}-N_{21}-O_{21}=n,$$

together with the same proviso when the sub-groups are completed, reproduces Bose's numbers just as well as his own rule. Even the new rule, however, can have no very profound meaning, since on inspecting the table, it is seen that either all the sub-groups are completed and so the total magnetic moment is zero, or all but one are completed and the moment of this one only comes into consideration.

The agreement between the calculated Bohr magneton numbers and the experimentally obtained Weiss magneton numbers is not satisfactory, but this is due rather to the present position of the quantum theory than to the particular ideas here discussed. To obtain the Weiss magneton numbers from the calculated Bohr values, Bose, similarly to Welo and Baudisch, makes use of the formula given by Sommerfeld in his 1923 paper. It would have been more in accord with the present state of the theory to have employed the later formula, $mg\sqrt{j\frac{j+1}{j}}$, from which the magnetic moment for an atom in any particular state can be calculated. The old formula is equivalent to assuming that the atom in question is in an 's' state. With regard to the present position of the theory and in view of our complete ignorance of the spectra of the doubly and trebly ionized atoms of the elements from Cr to Cu, it is probably

* *Zeit. f. Phys.* xxxv. p. 215 (1925).

better not to attempt to calculate the magneton numbers corresponding to any particular distribution of electrons. One must at present rather be satisfied with showing that those atoms which have the same magnetic properties have the same structure and that this structure is in general agreement with known facts, in particular that the atoms of diamagnetic compounds have the various sub-groups completed.

In his discussion of the magnetic properties of the coordination compounds, Cabrera has made use of the scheme put forward by Fowler. In this latter the electrons outside the K and L levels of a sixfold coordinating atom are supposed to tend to be distributed in the following groups :—8+6+12. The first 8 electrons are those occupying the M_{11}, M_{21}, and M_{22} sub-groups of the atom, the next 6 tend to collect into the M_{32} sub-group, and remaining 12 electrons are shared by the central atom and the groups surrounding it. These electrons are made up of those contributed by the various groups (their number can be calculated from Sidgwick's rules) together with the valency electrons of the central atom, *e.g.* in Fe^{++} 10+2, in Cr^{+++} 9+3. These electrons are probably arranged in 6 pairs of orbits and associated with the corners of a regular octahedron in agreement with the symmetry of the compounds according to Werner. This group of 12 electrons as a whole pos-esses no magnetic moment.

We thus have a very definite picture of the molecule, of the nature of the coordination number 6, and of the chemical bounds involved. The scheme thus possesses obvious advantages over schemes which involve distributing the "extra" electrons among the various atomic levels so as to make the central atom simulate the structure of some higher atom. As Fowler has pointed out, although the additional electrons might in certain compounds possibly be arranged in shells about the central atom somewhat as in a normal atom of higher atomic number, the orbits occupied by these electrons cannot be considered in the coordination compounds as in reality the same as the N_{11}, N_{21}, etc. orbits of a normal atom. Hence for this reason and because the schemes proposed by Welo and Baudisch and by Bose give no idea of the valency of the central coordinating atom nor of the coordination number of the compound, the scheme just discussed must be regarded as the most probable one.

We will now turn our attention to the ideas put forward by Cabrera to explain the magnetic properties of the

coordination compounds. The distribution of the electrons in the ions of the simple salts of the elements from Cr to Cu as proposed by Cabrera in accordance with the ideas of Stoner and Main-Smith is as follows :—

TABLE II.

Ion.	No. of electrons.				
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.
Cr^{+++}	2	2	4	–	3
Fe^{+++} Mn^{++}.....	2	2	4	1	4
Co^{+++} Fe^{++}.....	2	2	4	2	4
Co^{++}.....	2	2	4	2	5
Ni^{++}.....	2	2	4	2	6
Cu^{++}.....	2	2	4	4	5

This scheme is in agreement with the known magnetic properties of the simple salts of these elements, but the distributions must not be regarded as fixed with certainty.

For the distribution of the electrons in the ions of the sixfold coordination compounds Cabrera proposes the following scheme :—

TABLE III.

Ion.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Cr^{+++}	2	2	4	–	3	12
Co^{+++} Fe^{++} ...	2	2	4	–	6	12
Ni^{++}...	2	2	4	2	6	12

We see here the tendency of the M_{33} sub-group to fill to completion at the expense of M_{32}. In the case of Cr^{+++} there are no electrons in the M_{32} sub-group, so that M_{33} remains incomplete and the ion has the same structure as the ion in simple salts. In Co^{+++} and Fe^{++}, however, two electrons pass from the M_{32} to the M_{33} sub-group, making it

complete with 6 electrons. Since M_{33} is already complete in Ni^{++} no change takes place in this ion. On examining Table III. we see that it is to be expected that the sixfold coordination compounds of Cr^{+++} and Ni^{++} should have the same magneton numbers as the corresponding simple salts. This is actually the case. Again, the coordination compounds of Co^{+++} and Fe^{++} should be diamagnetic since M_{32} contains no electrons and M_{33} is complete. This also agrees with the facts.

Welo's determinations of the magnetic properties of the complex ferro- and ferricyanides had not been published when Cabrera's paper was written. It can, however, easily be seen that the scheme accounts for the properties of these compounds also. We may suppose that the M_{33} sub-group in the ferricyanides also tends to complete itself with 6 electrons. It can, however, only obtain 5, so that the distribution is as follows :—

Ion.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Fe^{+++}	2	2	4	–	5	12

We should therefore expect these substances to be paramagnetic and to possess a magneton number equal to that of the simple cupric salts, since the structures of the ions are the same except for the M_{32} sub-group. Since the latter is unoccupied in the ferricyanides and complete in the cupric salts, the net result is the same for both. Actually both groups of compounds contain approximately 10 Weiss magnetons.

Cabrera has also discussed the magnetic properties of the fourfold coordination compounds of Ni^{++} and Cu^{++}, and proposes the following scheme for the electron distribution.

Nucleus.	No. of electrons.					Binding electrons.
	M_{11}.	M_{21}.	M_{22}.	M_{32}.	M_{33}.	
Ni^{++}	2	2	4	4	4	8
Cu^{++}	2	2	4	4	5	8

In the case of the fourfold coordination compounds there are 8 binding electrons or four pairs, which, following

Werner and Sidgwick, are to be considered as associated with points lying, not at the corners of a tetrahedron, but in a plane and occupying, in the case of compounds in which the four groups are all the same, the corners of a square. Cabrera, arguing from analogy with the sixfold compounds, supposes that the M_{32} sub-group, which when complete possesses 4 electrons, will for this reason and because of the fourfold arrangement of the outer binding electrons tend to be completed at the expense of M_{33}. He therefore supposes that Ni^{++} has 4 electrons in both M_{32} and M_{33} in place of 2 in M_{32} and 6 in M_{33} as in the simple nickel salts. Since Cu^{++} already possesses 4 electrons in the M_{32} sub-group, the structure of this ion is the same in the fourfold co-ordination compounds and the simple cupric salts.

While this scheme may be said to give a fair account of the properties of the copper compounds, the complex compounds having a magneton number of about 9 and the simple salts of about 9·7, it does not seem so successful in the case of the nickel compounds. It would seem reasonable to expect that the 4.4 arrangement of the electrons would give a greater magneton number than the 2 6 arrangement of the simple salts. Actually the magneton number of the fourfold nickel compounds is about 13, while that of the simple nickel salts is 16. Cabrera admits that there are difficulties in the way of any scheme such as that which he proposes but considers that any different one, which would be successful for Ni^{++}, would probably encounter equal difficulties with Cu^{++}.

It would seem to the writer that a possible method of explaining the properties of the fourfold compounds is as follows. It may be quite possible that there is not the tendency of the M_{32} sub-group to be completed, as suggested by Cabrera, for the following reasons. Any tendency which the outer binding electrons will have in causing the M_{32} electrons to assume the symmetry of the former will be less than is the case for the M_{33} in the sixfold compounds, because the M_{32} electrons are to a certain extent shielded by the outer M_{33} electrons. Furthermore, it is quite possible that the symmetry of the 4 M_{32} electron orbits, when the sub-group is complete, is different from that of the outer binding electrons which are in one plane, the former possibly possessing tetrahedral symmetry. If it is allowed that these factors will reduce any tendency for the M_{32} sub-group to complete itself in the fourfold compounds, it will be seen then that the distributions of the electrons in the M_{32} and M_{33} sub-groups will be the same in the coordination compounds and the simple salts.

Since, however, these groups are surrounded in some way by the 8 binding electrons arranged in one plane, there is likely to be a strain or partial distortion of the symmetry of the M_{32} and M_{33} electron orbits, with a corresponding decrease in the magneton numbers compared with those of the simple salts. Actually there is a small decrease in the magneton numbers in both the nickel and the copper compounds, 13 in place of 16 and 9 in place of about 10 respectively. The strain postulated may be similar to that supposed to exist in unsaturated organic compounds, since the fourfold coordination compounds may be looked upon as unsaturated, for of the 6 corners of the octahedron of the sixfold compounds, 4 lying in one plane are occupied, but the axial positions are vacant.

Many more experimental data will be required before the properties of the fourfold compounds can be explained with any certainty. Rosenbohm only gives measurements for five such compounds of definitely known structure, two for nickel and three for copper. A further investigation of the magnetic properties of the coordination compounds, preferably over as extended a range of temperature as possible, would be of great value.

A point of great importance must be mentioned here. It will be noticed that in the three schemes considered above a distinction has been made between simple and complex salts and that this distinction has been retained so far in the discussion. Such a distinction cannot, however, be maintained. Thus, for example, the typical "simple" salt, $NiCl_2 . 6H_2O$, is according to Werner to be regarded as a sixfold coordination compound, and the formula is to be written $[Ni(OH_2)_6] . Cl_2$. The other "simple" salts also require to be interpreted in the light of such views. It will then be seen that the distinction made by Cabrera between the simple and complex salts, that in the latter there is a preferential completion of the M_{33} sub-group in the sixfold compounds, cannot be maintained. The hypothesis must be revised or altogether rejected. It is hoped to discuss the question from the point of view that the "simple" salts are in reality also coordination compounds in a further paper. The standpoint may be taken that the distributions of electrons proposed by Cabrera for the "simple" and the complex salts, with the suggested modification in the case of the fourfold compounds, are probably correct but that the reasons put forward in support of them require revision.

The Davy-Faraday Laboratory,
The Royal Institution,
Albemarle Street, London, W. 1.
Feb. 4th, 1926.

VII. *X-Ray Term Values, Absorption Limits, and Critical Potentials.*

By Edmund C. Stoner, *Ph.D.* (*Cambridge*), *Lecturer in Physics at the University of Leeds* *.

§ 1. Introduction.

During the last few years a large number of investigations have been made on the critical potentials for the excitation of soft X-rays in solid elements subjected to electronic bombardment. In the usual arrangement, electrons from a hot filament are accelerated towards a target under a variable applied voltage, and the photo-electric effect of the emitted radiation on a subsidiary electrode is measured. Precautions are taken to ensure the absence of effects due to electron scattering and secondary electron emission. The photo-electric current, expressed as a fraction of the primary current, is plotted against the accelerating voltage. The curves obtained usually show a number of more or less definite bends, and the corrected voltages at which these occur are taken to correspond to critical potentials for the excitation of X-rays. With a particular apparatus, the critical points are generally reproducible to one or two volts, and there can be little doubt as to their reality. The character of the bends, however, even for the same critical point, shows considerable variability, depending in some obscure manner on the precise conditions. Although different investigators' results may be in rough agreement as to some of the points, in general the agreement is far from complete, particularly as to the number of points observed.

Some of the critical points have been interpreted as corresponding to definite X-ray levels in the atoms, and it is the purpose of this paper to discuss how far this correlation is possible. As the number of critical points usually exceeds the number of energy levels, and as different investigations yield different values, the identification tends to become very arbitrary when applied to levels for which X-ray data are not available. In the interests of brevity, the discussion here will be mainly confined to the elements Cr (24) to Zn (30). The whole series have recently been investigated by Andrews, Davies and Horton [1], and particular members

* Communicated by Prof. Whiddington, F.R.S.

[1] Andrews, Davies and Horton, Proc. Roy. Soc. cx. p. 64 (1926).

by Thomas [2] (Fe, Co, Ni, Cu) and by Richardson and Chalklin [3] (Fe, Ni).

The measurements of the wave-lengths of some of the L series lines of these elements by Thoræus [4] enable fairly complete energy level schemes to be drawn up. Some of the difficulties which emerge in making computations of this kind, based on the combination principle, are discussed (§ 2).

The problem of the fine structure of X-ray absorption edges is next considered, partly for its own interest and partly because some attempts have been made to correlate the multiplicity of critical points with this fine structure [1] (§ 3).

The experimental critical potential results are briefly summarized (§ 4). Various interpretations which have been given are then discussed and some further suggestions are put forward (§ 5). The paper closes with a summary (§ 6).

§ 2. Computation of Term Values from X-Ray Data.

The term values for the energy levels expressed in Rydberg units which may be derived from the X-ray data are set out in Table I. for the elements Ti to Zn. The observed values for the K absorption limit are those of Lindh [5], Chamberlain [6], and Walter [7], which are believed to be the most accurate available. The values for the Kγ line are those of Siegbahn.

Under [K] are given the values for the K edge which have been taken as the basis of the subsequent calculations. In arriving at these values it has been assumed that they increase regularly in passing through the sequence of elements (actually $\sqrt{\frac{\nu}{R}}$ values were considered); consistent with this, values as close as possible to those observed have been taken. The procedure is slightly arbitrary, but seems justified by the fact that the [K] values do not differ from those observed by more than these differ from each other. (The precise significance of [K] will be considered in the next section.)

The values derived for the other levels depend essentially on those assumed for [K], and small relative errors in the determination of the K edge will result in large relative errors for the levels of smaller energy. It is probably for

[2] Thomas, Phys. Rev. xxv. p. 319, and xxvi. p. 739 (1925).
[3] Richardson and Chalklin, Proc. Roy. Soc. cx. p. 247 (1926).
[4] Thoræus, Phil. Mag. i. p. 312 (1926).
[5] Lindh, *Zeit. f. Phys.* xxxi. p. 210 (1925).
[6] Chamberlain, Phys. Rev. xxvi. p. 525 (1925).
[7] Walter, *Zeit. f. Phys.* xxx. p. 350 (1924).

TABLE I.—$\frac{\nu}{R}$ Term Values.

Element.	K observed.	Kγ.	[K].	L_I.	L_{II}.	L_{III}.	M_I.	$M_{II, III}$.	$M_{IV, V}$.
22 Ti ...	365·8 (L) 366·0 (C)	365·6	365·8	(41·0)	34·0	33·6		2·6	
23 V ...	402·7 (L) 402·9 (C)	402·4	402·7	(45·9)	38·5	38·0		3·0	
24 Cr...	441·0 (L) 441·3 (C)	440·9	441·3	(51·0)	43·2	42·5	(5·9)	[3·7]	·2
25 Mn .	481·6 (L)	481·3	481·7	(56·3)	(48·1)	47·2	(6·2)	3·6	·2
26 Fe...	523·5 (L)	523·5	523·8	(61·9)	53·2	52·2	6·9	4·0	·3
27 Co...		567·6	567·8	(67·7)	58·6	57·4	7·3	4·3	·3
28 Ni ...	613·8 (W)	613·5	613·8	(73·8)	64·3	63·0	7·9	5·1	·3
29 Cu...		661·3	661·7	(80·3)	70·4	68·9	8·9	5·8	·4
30 Zn...	711·4 (W)	711·3	711·5	(87·2)	(76·9)	75·2	9·9	6·6	·7

this reason that the $M_{II,III}$ values for these elements in the original Bohr and Coster tables show such marked irregularities.

Walter[8] has drawn up a fairly complete energy-level scheme for the elements Ti (22) to Te (52) from the wave-length data then available. Recognizing the lack of precision in some of the K edge wave-length measurements, he computed [K] by assuming that it exceeded Kγ by a fractional amount p:

$$\left(\frac{\nu}{R}\right)_K = \left(\frac{\nu}{R}\right)_{K\gamma}\left(\frac{100+p}{100}\right).$$

On the basis of measurements for Ni, Rh, and W, Walter assumed that p varied linearly with atomic number:

$$p = \cdot 010\,(Z-22).$$

The Kγ line corresponds to the transition $N_{1,1} \rightarrow K$, so that it is virtually assumed that the level (which may be the boundary of the atom) to which the electron is removed in the K-edge transition differs from $N_{II,III}$ by an amount which increases regularly from zero for Ti. This assumption seems difficult to justify for elements such as those here in question, in which $N_{II,III}$ is a virtual level, though a linear relation of the kind employed may hold roughly for elements of higher atomic number than those in which the $N_{II,III}$ levels are first fully occupied. It is true that the [K] values obtained in this way will differ relatively little from those in the [K] column of Table I. (as may be seen from the values there given for the Kγ lines); but the procedure is somewhat unsatisfactory, and it seems better to take [K] values based on those actually observed for elements for which precise measurements have been made—particularly as the Kγ line, as has been pointed out by Coster[9], is very weak and difficult to measure accurately for elements of low atomic number.

In the computation of the other levels, the following combination equations have been used:—

$$\begin{aligned}
L_{III} &= K - K\alpha_1,\\
L_{II} &= K - K\alpha_2,\\
M_{II,III} &= K - K\beta,\\
M_I &= L_{II} - Ll = L_{III} - L\eta,\\
M_{III\,V} &= L_{III} - L\alpha = L_{II} - L\beta_1.
\end{aligned}$$

[8] Walter, *Zeit. f. Phys.* xxx. p. 357 (1924).
[9] Coster, *Zeit. f. Phys.* xxxi. p. 898 (1925).

The $\frac{\nu}{R}$ values of the K lines have been taken from the tables in Sommerfeld's *Atombau* (4th ed. 1925, p. 260).—For these elements the measurements are mainly those of Siegbahn. The L-line values are taken from Thoræus [4], who has measured $L\alpha$ and $L\beta$ for Cr to Zn, and $L\eta$ and Ll for Fe to Zn. The bracketed values for M_I for Cr and Mn are extrapolated. For the calculation of L_I, the $L\beta_3$ and $L\beta_4$ lines are required ($L\beta_3 = L_I - M_{III}$, $L\beta_4 = L - M_{II}$), and these have not yet been measured. In order to obtain an estimate of L_I, it has been assumed that L_I and L_{II} form a normal screening doublet, the separation being given by

$$\sqrt{L_I} - \sqrt{L_{II}} = 0{\cdot}57$$

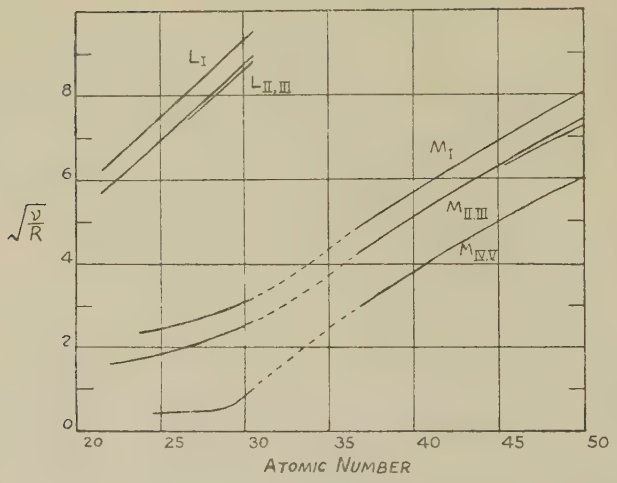
(*cf.* Sommerfeld, p. 458).

The numbers so obtained show a fairly regular progression with atomic number, except in the case of $M_{II, III}$ for Cr. Slight irregularities may be real—though little can be said with certainty on this point at present,—but the divergence in this case is so large that it is probably to be attributed to some error in the measurements. There can be little doubt as to the substantial accuracy of the general order of magnitude of the term values deduced and as to their sequence. The M_I and $M_{II, III}$ values are coherent with those of elements of higher atomic number, as is shown by plotting $\sqrt{\frac{\nu}{R}}$ (see fig. 1). (Walter's values are taken for elements of higher atomic number.) There is no indication of unexpected peculiarities in the curves in this region such as are suggested by some of the values which have been attributed to the levels on the basis of critical potential measurements. (See, for example, the curves given by Sommerfeld, p. 572.)

The most definite value for the $M_{II, III}$ level in this region is probably that deduced by Millikan and Bowen [10] from lines in the ultra-violet spectrum of Ca (20). They give for M_{II}, $\frac{\nu}{R} = 1{\cdot}8387$, $\sqrt{\frac{\nu}{R}} = 1{\cdot}3560$; for M_{III}, $\frac{\nu}{R} = 1{\cdot}8104$, $\sqrt{\frac{\nu}{R}} = 1{\cdot}3455$. These values fall in line with those of Table I.

[10] Millikan and Bowen, Phys. Rev. xxiii. p. 1 (1924).

Fig. 1.—$\sqrt{\frac{\nu}{R}}$ Values for Terms.



In Table II. the term values required in the critical potential discussion are given in volts $\left(V = 13{\cdot}54\frac{\nu}{R}\right)$. An interpolated value has been used for Cr $M_{II,\,III}$ corresponding to 3·4 in Table I. in place of 3·7.

Table II.—Term Values. Volts.

Element.	L_I.	L_{II}.	L_{III}.	M_I.	$M_{II,\,III}$.
24 Cr ...				(80)	(46)
25 Mn...				(84)	49
26 Fe ...	(838)	720	706	93	54
27 Co ...	(917)	793	777	99	58
28 Ni ...	(999)	871	835	107	69
29 Cu ...	(1124)	953	933	120	78
30 Zn ...				134	89

§ 3. The Fine Structure of X-Ray Absorption Edges.

It was at first believed that X-ray absorption edges were simple in structure, there being a sudden increase in absorption, followed by a gradual falling off, as the frequency of the incident radiation increased, passing through the critical frequency corresponding to the energy required to remove an electron from a level completely out of the atom (that is, to give it a total energy greater than zero). Photographic investigations of Fricke, Lindh, and others showed that in many cases the long wave-length edge was marked by an absorption line followed by one or more regions of weaker and stronger absorption before the uniform continuous absorption region was reached. Kossel had predicted that a fine structure should be found, corresponding to the removal of the electron to various possible virtual (optical) orbits at frequencies lower than that at which continuous absorption began. This interpretation has been generally accepted, but it does not seem to have been brought into any close relation with the fine structures actually observed, and it seems desirable to consider the observations and theory somewhat more closely, particularly in regard to the order of magnitude of the separations of the "remarkable points" of the fine structure.

When pure elements are examined, at least when these are metallic, in general no fine structure is observed. This statement is supported by the work of Fricke [11] (Mg, Al), Lindh [5] (Ti, V, Cr, Mn, Fe), and Chamberlain [6] (Ti, V, Cr).

For elements such as P, S [11], and Cl [12], however, whose molecules are polyatomic, fine structure is found. The fact that a fine structure is not observed for metallic elements—whose molecules in general may be regarded as monatomic, and as not being markedly distorted from their "free state" form as regards level energies—does not necessarily mean that it is non-existent, but that it is confined within a range of wave-lengths which is so small that it is unresolved, owing to slit widths, slight non-homogeneity of the radiation components, and scattering. On Fricke's photographs the distance of the point at which increased absorption begins to the point at which it is a maximum corresponds to 2·7 and 4·9 volts for Mg and Al respectively. Richtmyer [13] has recently considered in great detail the correction necessary

[11] Fricke, Phys. Rev. xvi. p. 202 (1920).

[12] The case of S and Cl is discussed in detail by Siegbahn: Spectroscopy of X-Rays, Eng. transl. p. 143 (Oxford, 1924).

[13] Richtmyer, Phys. Rev. xxvi. p. 724 (1925).

for finite slit width ; he concludes from his measurements (by the ionization method) of absorption near the AgK limit that the jump occurs within ·0002 A.U. This, though small (about ·04 per cent. λ_K), corresponds to a voltage range of about 10, which is of the order of magnitude of the optical energy level differences.

With compounds, the continuous absorption edge is shifted to a shorter wave-length, but on the long wave-length side of this a white absorption line is generally found (Coster[14], Lindh[5], Chamberlain[6]). Within the limits of experimental error the long wave-length edge of the absorption line coincides with the wave-length of the absorption edge of the free element. It has been supposed that the white line is actually due to the free element which may be present owing to oxidation or reduction processes brought about by the X-rays themselves, and Chamberlain brings forward some evidence in support of this view. The persistence of the white line and its intensity, however, in many cases where the amount of free element present must be very small, suggests that it may be an essential characteristic of the absorption of the compound, though its intensity may be increased if some of the free element is present as well. Thus Nishina[15] finds an intense white line characterizing the L_{III} absorption edge of compounds of the trivalent elements in the group Pr (59) to Ho (67) ; there is a second white line on the short wave-length side ; and sometimes a third more diffuse line of still shorter wave-length is measurable.

The order of magnitude of the separation between the long wave-length edge of the white absorption line (K_1), corresponding to the edge for the free element, and the continuous absorption edge (K_2) on the short wave-length side may be illustrated by some values (in volts) given by Lindh.

Table III. shows clearly the dependence of the separation K_2-K_1 (or the shift of K_2) on the valency of the element concerned. The higher the valency the greater the separation. This correlation has been recognized for some time (Lindh, Siegbahn), but its significance in providing a possible clue to the fine structure problem does not seem to have been fully realized.

There can be little doubt as to the theoretical soundness of

[14] Coster, *Zeit. f. Phys.* xxv. p. 88 (1924).
[15] Nishina, Phil. Mag. xiix. p. 521 (1925).

Kessel's view, and this must form the basis of any explanation. For the normal atom the lowest frequency radiation which can remove an electron from a K level will be that with the quantum energy corresponding to the transition from the K level to the lowermost unoccupied virtual orbit to which a transition can occur—that is, in general, to the *np* optical orbit with the smallest *n*. Such an orbit may conveniently be referred to as "peripheral," and the energy of an electron in it will not differ widely from that of the most loosely bound electrons in the atom.

TABLE III.

$K_2 - K_1$. Volts. (Lindh.)

TiO_2.....	17·0	$MnSO_4$.....	9·7
V_2O_5	14·0	MnO_2	15·2
$Cr_2(SO_4)_3$...	11·9	$KMnO_4$ ...	20·0
$K_2Cr_2O_7$ ...	19·7	$FeSO_4$	9·0
		$Fe_2(SO_4)_3$..	13·9

Transitions should then be possible to *np* orbits of higher *n*; there should be a series of absorption lines crowding together to a head where continuous absorption begins, corresponding to the removal of the K electron to the "boundary" of the atom. By analogy with optical spectra, however, it may be supposed that the probability of absorption of the first line is much greater than that of higher members. The structure anticipated for a K edge would then be, proceeding from longer to shorter wave-lengths, an absorption line followed by a region of smaller absorption which increases to the head where continuous absorption begins and then falls off gradually. The line absorption, however, has not been definitely observed for pure elements. If the above view is correct, this is due to the fine structure region being so small that resolution is not obtained. The "fine structure range," as it may be called, will depend on the energy of the lowermost *np* term to

which a transition is possible. The order of magnitude of this may be readily calculated from the optical data. Thus for Mg the singlet and triplet $3p$ terms have energies corresponding to 3·3 and 4·9 volts. A fine structure within this range would hardly be observed. For ionized atoms, however, the fine structure range would be much increased. This may be illustrated by considering the energies of the lowermost optical p terms in a series of atoms :—

Approximate Energies of Lowermost Optical p terms.

($n=3$.) Volts.

Na 3 Mg^{+} 11 Al^{++} 21 Si^{+++} 34

Ionization would result in an increase in the fine structure range, with an increased possibility of resolution.

The above numbers can only be regarded as giving a rough idea of the order of magnitude to be expected, for although the field round an ion in a solid compound (*e.g.* round Mn^{++++} in MnO_2) will approximate to that round a free ion, it will be modified by the influence of the neighbouring ions of opposite charge.

That the "white line" should occupy approximately the same position for compounds in which the element has different valencies, and that this coincides with the edge for the free element, is readily intelligible.—The work required to remove a K electron to the boundary of an atom may be regarded as made up of that required to remove it to the peripheral orbit together with that to remove it from the "periphery" to the "boundary"; the first part will be little changed, as outer electrons, normally moving in peripheral orbits, are removed in different stages of ionization (or with increasing valency), but the second part will increase (with increase in the field beyond the periphery). In particular, the first part will be more nearly constant the larger the number of electrons moving in peripheral orbits of approximately equal energy.

The view that the K edge, as ordinarily measured, does not correspond to complete ionization is supported by the fact that when the energy of the $M_{IV,V}$ level for the first series of transition elements is calculated from the X-ray data (see Table I.). it comes out to be considerably smaller than would be anticipated from the optical spectra data. Thus the energies of the levels calculated will all be smaller than those corresponding to complete removal of an electron from them

to the boundary by a quantity of the order of a few volts. The exact quantity could only be calculated if the precise nk level to which the K electron is removed were known, and if the energy of this could be calculated from the optical spectra.

The question arises as to what is the lowest peripheral level to which a K electron may be removed in the neutral atom. Normally it would be expected that it would be a level for which $k=2$: for the elements here considered, the $N_{II, III}$ level. The absorption line would not then necessarily be of the same wave-length as Kγ, for the Kγ line is usually supposed to be due to a transition in an atom which has completely lost a K electron, so that Kγ would be of slightly longer wave-length than the absorption line. The problem, however, is complicated by the fact that the usual classification of X-ray levels (*e. g.* with five M levels, with $k=1$ for M_I, $k=2$ for $M_{II, III}$, $k=3$ for $M_{IV, V}$) only holds when these levels have their full complement of electrons. For the transition elements the $M_{IV, V}$ levels are being built up, and the N levels contain only a few electrons (usually one or two). The appropriate k values are in the nature of resultants (denoted by l in the recent work of Heisenberg and Hund), so that a number of electrons each characterized by $k=3$ may give rise to a configuration corresponding not only to D terms, but also to S, P, F, etc. This has a close connexion with the fact that changes of configuration involving double electron jumps may occur. The determination of the precise nature of the lowermost level to which a K electron can be transferred by the absorption of radiation must therefore await further developments in the analysis and interpretation of the optical spectra of the elements concerned.

As already mentioned, Nishina's observations on the structure of the L_{III} edge for Ho [15] ($Ho_2(SO_4)_3$ + aq. was used as the absorbing substance), three components were found; the separations being 34 and 89 volts. This would seem to require a more complicated explanation than that given above for the K edges of the elements of lower atomic number, and is left as an unsolved problem. The structure is possibly to be correlated with the fact that in the rare earth elements there are a number of levels (in the N, O, P groups) in an incomplete state, so that there are a greater number of possibilities of transition to levels which, in the ionized atom, may differ considerably in energy.

§ 4. Critical Potentials. Experimental Results.

The critical potentials found in recent investigations by a number of workers for the elements here considered are set out in the following tables.

Table IV a.

Critical Potentials for Cr to Zn.

Andrews, Davies, and Horton [1] (below 230 volts).

	g.	*f.*	*e.*	*d.*	*c.*	*b.*	*a.*
24 Cr		60	70		143	160	173
25 Mn		68	83	100	152	174	184
26 Fe	47	73	90	106	166	181	
27 Co			94	113	171	191	
28 Ni			104		178	196	
29 Cu			112		193	206	
30 Zn			119		200	214	

Table IV b.

Critical Potentials for Fe to Cu.

Thomas [2] (above 350 volts).
Rollefson [16] (600–700 volts).

Fe (T.)		639	704	818	
„ (R.)	618	637	697		
Co (T.)		705	764	873	950
Ni (T.)		774	833	948	1017
Cu (T.)		820	929	1017	

Table IV c.

Critical Potentials for Iron.

Tables IV c and IV d :—
Richardson and Chalklin [3] (40–600 volts).
Rollefson [16] (30–185 volts).
Chu [17] (0–120 volts).

R. and C.	46	51	64	76		85	95	108	115		138
Rollefson	47				82		95			130	
Chu		52	68		80						
R. and C.						190	221	241	270	288	498
Rollefson	141	147	153	160							

Table IV d.

Critical Potentials for Nickel.

R. and C.	39?			80?	89	99	140	245	316	335?
								393?	433?	532?
Chu		49	75			98				

[16] Rollefson, Phys. Rev. xxiii. p. 35 (1924).
[17] Chu, Journ. Franklin Inst. 200. p. 629 (1925).

The above tables summarize only a few of the investigations which have been made, but they will be sufficient to serve as a basis for the consideration of the general character and coherence of the results. (For a comprehensive survey of the values obtained by different workers for Fe and Ni, Richardson and Chalklin's paper may be consulted, and that of Andrews, Davies, and Horton for the elements of Table IV A, below 230 volts.)

It should first be noted that the number of critical points found varies very greatly. Thomas, working with large thermionic currents (·5 to 4 milliampere), taking great precautions to ensure steadiness, and varying the voltage by small intervals, obtained over forty breaks in the curves for Fe, Co, and Ni below 350 volts, and over twenty for Cu below 90 volts. These breaks were interpreted as ionization or resonance breaks according as the portion of the curve above showed an upward or downward concavity. In view of Richardson's observations that the character of a break may vary considerably in different experiments, it seems doubtful whether the classification has any significance, though Thomas found that the curves were closely reproducible. In distinction to Thomas, Chu, working with small thermionic currents (of the order of 10 microamperes), found well-defined breaks, few in number, as indicated in the above tables. (Only three were found for Fe and Ni, and five for Cu—at 30, 49, 62, 79, and 90 volts.)

Owing to the large number of breaks found by Thomas, some of his values may usually be found fairly close to those of other observers; but when experiments in which the number of critical points is more limited are compared with each other, there is so little general agreement that it almost seems as if agreement is fortuitous even when it does occur. This is seen at once by inspection of Tables IV A, C, and D. For iron there is some agreement as to a critical point in the neighbourhood of 50 volts, but otherwise it is only by considerable forcing that the results can be regarded as mutually supporting. This cannot be attributed to errors in correcting the measured voltage for initial velocity, and for the work function, for there is disagreement as to the sequence of values as well as their absolute magnitude. It is clear that the critical potentials, at least in the low voltage region, do not yield direct and simple information as to the soft X-ray energy levels in atoms. They must, however, have some connexion with them, and some of the suggestions which have been made will now be considered.

§ 5. Critical Potentials. Suggested Interpretations.

As Andrews, Davies, and Horton have examined the longest sequence of elements, their interpretations of their results will be considered first. They suggest that the points *g*, *f*, and *e* (Table IV A) are associated with transitions from the $M_{II, III}$, and the points *d*, *c*, *b*, *a* from the M_I level; *g* and *d* corresponding to transitions to the periphery, and the other points to virtual orbits beyond the periphery. The consideration of the magnitudes of the differences of energy associated with such transitions in § 3, however, casts doubt on this interpretation. The range of voltage for one set of transitions should not be greater than the fine structure range (depending on the energy of the lowermost unoccupied optical level), and this for the *neutral* atom is of the order of a few volts. On the interpretation given, moreover, the work required to remove an $M_{II, III}$ electron to the boundary would correspond in the case of iron, for example, to the limit of the series 47, 73, 90—it would be greater than 90 volts: similarly, the $M_I \rightarrow$ boundary transition would correspond to an energy greater than 180 volts. (The limit of the series 106, 166, 181.) Both of these values are far in excess of those calculated from the X-ray data (Table II.). There are thus two reasons indicating that the view requires considerable modification.

Other workers have also attempted to account for the critical points in a general way as associated with ionization and resonance transitions. Richardson and Chalklin have made the additional suggestion that transitions may be possible to orbits within the atom which are normally unoccupied. It must be remembered, however, that the last bound electrons enter orbits in which they are most firmly bound, so that the postulate of unoccupied orbits having greater (negative) energy—which is necessary if the hypothesis is to explain a wider range of facts than the usual one—raises many difficulties. A further suggestion of Richardson and Chalklin's—that there may be discontinuities in the general radiation—is so far without independent experimental support.

Multiple impact, as has been mentioned by Thomas and others, will account for critical potentials which are the sum of those corresponding to single impact critical potentials—an electron having sufficient energy, after a "resonance" encounter, to produce ionization or resonance in another atom.

The suggestions so far considered would lead to the

anticipation of critical potentials crowded together near X-ray energy level values (corresponding to the narrow virtual orbit and fine structure range), and of potentials which are the sum of these. They do not, however, seem capable of explaining many of the relatively widely spaced points which are observed.

A comparison of Tables IV. and II. shows that critical potentials are sometimes observed which can be fairly definitely associated with X-ray levels. In Thomas's results it is particularly striking that although he found a large number of breaks at lower potentials, above 350 volts he found only those recorded in Table IV B. (It should be noted, however, that Richardson found a few breaks in the intermediate region for Fe and Ni, though he regards those for Ni as doubtful.) Of these the series, for Fe, Co, Ni, and Cu, of 704, 764, 833, and 929 agree reasonably well with the values 706, 777, 853, and 933 computed for L_{III} from the X-ray data. The next group of values are considerably above those computed for L_{II}, and rather smaller than those for L_I ; while the largest critical potentials observed (950 for Co, and 1017 for Ni) are larger than the L_I values (approximately 917 and 999). As to the M levels, Horton's g value for iron of 47, with those of other observers (Table IV C) of 46, 47, 51, and 52, agree fairly well with the computed value of 54 for the $M_{II, III}$ level ; but in the absence or disagreement of the corresponding point for Ni this is not very satisfying. Horton's e values are fairly close to those computed for M_I, but are consistently lower by an average value of about 5 volts.

Critical potentials are undoubtedly to be associated with transitions of electrons from particular levels ; and some of the higher values found (such as Horton's a, b, c groups) must be due to multiple impact. The problem which remains is to account for some of the higher values found where multiple impact seems inadequate to explain the values even qualitatively, and to account for values much lower (such as some of those of Thomas in the L region) than the computed term values.

The suggestion is made that an explanation of many of the apparently anomalous results is to be sought in the consideration of the excitation potentials of atoms which have already lost one or more electrons, either from loosely bound groups, or from groups more "deeply seated" in the atom. Under the experimental conditions there must generally be present atoms which have lost a number of outer electrons. As discussed in § 3, the amount of work then

required to remove an electron from, say, the K level completely to the boundary of the atom will increase in passing from the neutral to the singly, doubly, ... charged atom by an amount approximately equal to that required to remove the series electron from the atom in its different stages of ionization; these differences being of the same order of magnitude as those observed in the experiments. A simple correlation of the results is, however, hardly feasible owing to the many different possibilities, the inadequacy of the optical spectra data, and the indefinite experimental conditions. If electrons have been removed from say an M level, then the possibility arises of there being a critical potential corresponding to the removal of an L electron to the vacant space created. This potential will be lower than the L critical potential by an amount approximately equal to that of the M level concerned. Some of Thomas's L values are in rough agreement with this view. The critical potentials will not necessarily agree with X-ray line values owing to the complicated reorganization processes which may occur.

The ionization of a particular atom may be brought about not only by direct impact, but by absorption of radiation from other atoms. This makes an additional complication, for it means that it will be almost impossible from critical potential experiments alone, even if multiple impact effects could be excluded, to obtain any precise idea of the energy levels, unless there is some information available as to their order of magnitude from spectroscopic data—particularly in the case of the levels of smaller energy. It would seem that experiments in which the primary current density is as small as possible would lead to fewer breaks being observed, which might be more easily interpreted; but the technical difficulties would then become greater. The whole question of the relative probability of single and multiple impact and multiple excitation effects is involved.

The recent development of the technique for the investigation of long X-rays and short ultra-violet rays means that data will soon be available from which more complete and accurate energy level schemes may be drawn up. Apart from this, the most direct way of investigating the energy level values is probably that of measuring the lines in the magnetic spectrum of the electrons emitted photo-electrically under the influence of monochromatic incident radiation as used so successfully by Robinson, Whiddington, de Broglie, and others. (If the precision and resolving power could be sufficiently increased, such investigations should also be able to shed further light on the fine structure problem, for it is the energy required to remove an electron completely from

the atom which can be determined.) Critical potential investigations, carried out under well defined conditions, will then become of great interest and value in connexion with many problems, though they do not seem adapted for the direct precise determination of energy level values.

§ 6. Summary.

The paper deals with term values, absorption limits, and critical potentials, with particular reference to the elements titanium (22) to zinc (30).

The term values are computed from the X-ray data, and are shown to fit in coherently with those of elements of higher and lower atomic number. The limitations of the method are considered.

The fine structure of absorption edges is discussed, and it is concluded that the term values correspond to the energy required to remove an electron to the lowermost possible unoccupied optical level in the atom. For a neutral atom this will differ by only a few volts from that corresponding to removal to the boundary, but the difference increases with successive stages of ionization of the atom. This is correlated with the range of fine structure observed for compounds. The general character of the edges, and the order of magnitude of the separations between the fine structure components are accounted for.

The critical potential results of a number of investigators are compared, and some of their interpretations criticised. In addition to the usual explanations, it is suggested that some of the points correspond to critical potentials for atoms which have been ionized by the loss of outer or inner electrons. These potentials may be higher or lower than those for the neutral atoms. It is shown that critical potential experiments are unsuitable for the direct precise determination of atomic level energy values, particularly when these are small.

Department of Physics,
University of Leeds.
March, 1926.

Note added to proof.—Using high resolving power, Coster and van der Tuuk ('Nature,' cxvii. p. 586, April 24, 1926) have recently found fine structure in the K absorption edge of argon. They consider that this is probably to be explained as due to transitions to different p levels, the separation of the two edges observed (about 1·7 volts) being of the right order of magnitude. The interpretation is in agreement with that of § 3.

VIII. *The Crystalline Structure of Anhydrite.* *By* E. C. S. Dickson, *B.A., Ph.D., Senior Lecturer in Physics, Manchester University, and* W. Binks, *B.Sc. Manchester* *.

1. ANHYDRITE, the stable form of anhydrous calcium sulphate $CaSO_4$, crystallizes in the bipyramidal class of the rhombic system. Its axial ratios are given by von Groth as

$$a : b : c = 0{\cdot}8932 : 1 : 1{\cdot}0008.$$

Natural crystals generally show only the three pinacoid faces : cleavage parallel to the (010) and (001) faces being perfect, and parallel to the (100) face less perfect. The specific gravity is 2·96.

The pseudo-tetragonal axial ratio $b : c$ distinguishes anhydrite from the chemically analogous substances barytes, celestine, and anglesite, the structures of which have been determined by James and Wood †. Its structure might therefore be expected to be relatively simple, and to throw further light on the dimensions of the SO_4 group, which has been shown by Bradley ‡ to approximate to a tetrahedron, the centres of the oxygen atoms lying at the corners and the sulphur atom at the centre, the distance S to O being about 1·5 to 1·6 Å.

2. *Experimental Results.*

Natural crystals from various sources were examined by the usual ionization spectrometer method. Cleavage faces were lightly ground before use, the other faces being ground on the crystals with carborundum. It was found convenient to embed the crystal entirely in a mass of dental wax before grinding, to prevent shattering of the face.

All intensities were compared ultimately with that of a standard (400) rock-salt reflexion (actual second order reflexion), but substandards were employed for some of the weaker spectra. Owing to the small size of some of the faces available the accuracy of the intensity measurements, especially at low angles of incidence, is questionable. K_α radiation from a molybdenum Coolidge bulb was employed throughout.

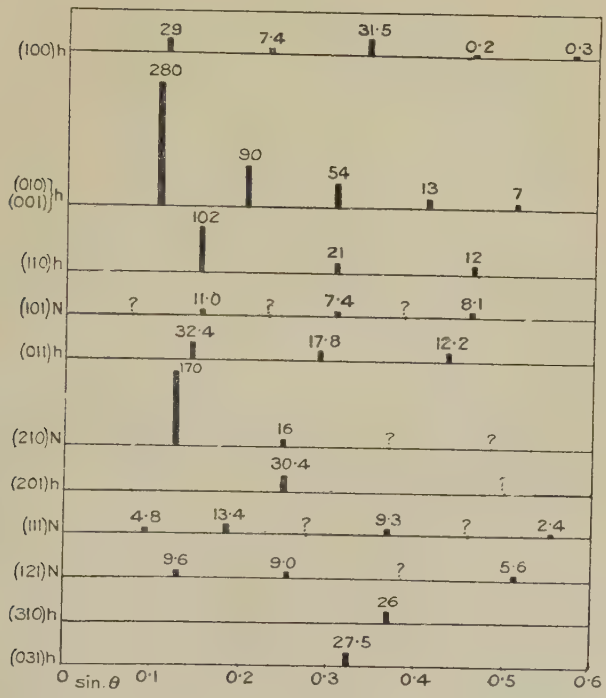
* Communicated by Prof. W. L. Bragg, M.A., F.R.S.
† Proc. Roy. Soc. cix. p. 598 (1925).
‡ Phil. Mag. xlix. p. 1225 (1925).

The following is a list of the faces examined :—

(100)	(110)	(210)	(031),
(010)	(101)	(201)	(111),
(001)	(011)	(301)	(121).

Fig. 1 shows graphically the distribution and intensity of the observed reflexions.

Fig. 1.



3. *Unit Cell and Space-Group.*

During the course of the present work a determination of the unit cell and space-group of anhydrite was published by Rinne, Hentschel, and Schiebold *. Their values for the dimensions of the unit cell are

$$a = 6{\cdot}21 \text{ Å}. \quad b = 6{\cdot}95 \text{ Å}. \quad c = 6{\cdot}96 \text{ Å}.$$

The corresponding values from measurements made by us during a preliminary survey of the crystal are :

$$a = 6{\cdot}19 \text{ Å}. \quad b = 6{\cdot}94 \text{ Å}. \quad c = 6{\cdot}94 \text{ Å}.$$

* *Zeitschr. f. Krist.* lxi. p. 164 (1925).

We do not regard our figures however as very reliable, and in our determination of the crystal structure we have used the former values.

The specific gravity shows that the cell contains four molecules.

Using the rotating crystal method, Rinne, Hentschel, and Schiebold identified the space-group of anhydrite as V_h^{17} in Schönflies's notation. The spectrometer measurements made by us are not sufficient for a unique determination of the group but they agree, as far as they go, with the exception of the (101) face. We were unable to detect the odd spectra from this face with our apparatus, so that only even spectra appeared to be present. Rinne, Hentschel, and Schiebold record the presence of a (303) reflexion, but qualify it as not quite certain.

Further corroboration of the space-group was obtained by means of a Debye powder-photograph, kindly taken for us by Dr. A. J. Bradley. It happens by chance that although the pseudo-tetragonal ratio of the *b* and *c* axes causes reflexions from certain faces to coincide on the powder-photograph, yet the presence or absence of certain lines provides useful criteria which confirm the space-group as V_h^{17}.

It must be remembered that, in the case of a Laue photograph of a single crystal, the pseudo-tetragonal ratio of the axes will be masked entirely by the true rhombic nature of the crystal, as can be seen by inspection of such photographs of anhydrite already published by Haga and Jaeger *, and by Rinne †. The Laue diagrams show only two planes of symmetry at right angles.

Astbury and Yardley ‡ give the following criteria for the abnormal spacing of planes in the group V_h^{17} (their Q_h^{17}, when their axes are suitably transformed to fit the crystallographic axes of anhydrite.

All spacings of the general type $(h\,k\,l)$ are halved if $h+l$ is odd.

All $(o\,k\,l)$ spacings are halved.

4. *Symmetry Elements of the Group* V_h^{17}.

The symmetry elements of the group are given in full in Rinne, Hentschel, and Schiebold's paper § and in the tables of Niggli or Astbury and Yardley.

* *Akad. v. Wetensch. Amst.* xxiv. p. 460 (1915).

† II. *Mitteil. Ber. d. Sachs. Akad. d. Wissensch.* lxviii. p. 11 (1915).

‡ Phil. Trans. Roy. Soc. A, ccxxiv. p. 225 (1924).

§ *Loc. cit.* The reflexion planes given as $(010)_0$ $(010)_{\frac{1}{2}}$ should read $(001)_0$ $(001)_{\frac{1}{2}}$, and the symmetry centres printed as $[[\frac{1}{4}\ \frac{1}{2}\ \frac{3}{4}]]$, $[[\frac{3}{4}\ \frac{1}{2}\ \frac{3}{4}]]$, should not have the minus signs.

The most important feature is the presence of two sets of intersecting reflexion planes, $(001)_0$ $(001)_{\frac{1}{2}}$ and $(010)_{\frac{1}{4}}$ $(010)_{\frac{3}{4}}$. Three sets of glide planes also occur: $(100)_0$ $(100)_{\frac{1}{2}}$; $(100)_{\frac{1}{4}}$ $(100)_{\frac{3}{4}}$; $(001)_{\frac{1}{4}}$ $(001)_{\frac{3}{4}}$ with glides of $b/2$; $(b+c)/2$; $a/2$ respectively. The positions of most of the symmetry centres, which are of three types, and of the digonal rotation and screw axes are shown in figs. 2 and 3, in Astbury and Yardley's notation.

5. *Possible Crystal Structures.*

The only attempt yet made to assign a structure to anhydrite, so far as we know, is an admittedly conjectural one used in a diagram by Rinne * merely to illustrate the transformation into the unstable β-modification. In this diagram the SO_4 group appears to be represented as having all its atoms in one plane parallel to one of the pinacoids, while the calciums and SO_4 groups are arranged on two interpenetrating face-centred lattices.

Such a structure would require the spectra from one pinacoid face to be normal in intensity, since all the atoms are concentrated in the planes, while the normal character of the reflexions from the two other pinacoids would be relatively weakened by oxygen atoms lying off the planes. Reference to fig. 1 shows that the outstanding feature of the observed intensities is the presence of identical reflexions from two of the pinacoids, approximating to normal type, while the third pinacoid yields spectra so far from normal that the sixth order (third actual spectrum) is larger than the second (first actual spectrum).

This arrangement would therefore not correspond to the facts.

If now we start with the assumption of a tetrahedral SO_4 group, as already found in the structure of lithium-potassium sulphate and in barytes, celestine, and anglesite, we can make certain deductions as to permissible positions of atoms in the unit cell from symmetry considerations alone.

The peculiar symmetry of a tetrahedron precludes placing the sulphur atom which occupies its centre at a centre of symmetry of the space-group. The only other possible arrangement of four atoms in the unit cell of this space-group, is to place them so that each atom lies on both sets of reflexion planes, *i. e.* on their line of intersection, with one degree of freedom only.

* *N. Jahrb. f. Min.* ii. p. 98 (1916).

As regards the position of the sixteen oxygen atoms, we might try to place them at the sixteen centres of symmetry. These centres, however, are situated on parallel planes $(010)_0$ and $(010)_{\frac{1}{2}}$, while the intersections of the reflexion planes, on which the S atoms are located, lie a quarter and three quarters along the b axis of the cell. On plotting the position of the centres, it is seen that no arrangement of four independent tetrahedra is possible, and this arrangement is also incompatible with the observed intensities from the (010) face.

It might still be possible for either eight or four oxygen atoms to be disposed in four separate manners at the three types of symmetry centre available (one eight-fold, two four-fold).

Now the eight-fold symmetry centres common to the unit lie at the corners of two contiguous parallelepipeds, and could only be regarded as forming pairs of interpenetrating tetrahedra, which would require the two sulphur atoms in each pair to occupy the same portion of space. These eight oxygen atoms would also be out of phase with the sulphurs for the (020) and (002) reflexions.

The positions of both sets of four-fold centres are such that they could not be grouped in tetrahedra round the S atoms. They would also be in phase with the S atoms for the (002) and out of phase for the (020) reflexions, rendering these spectra unlike. It appears then that none of the oxygen atoms can be at a symmetry centre.

An oxygen atom placed in a general position in the cell with coordinates $[[m, n, p]]$ introduces sixteen by the operations of symmetry. But if the position of these points is plotted, it is found that they cannot be arranged in tetrahedra with centres on the intersection of the reflexion planes.

The oxygens must therefore have either one or two degrees of freedom only.

Points with one degree of freedom may occupy two sets of positions. A four-fold one with coordinates $[[n, \frac{1}{4}, 0]]$; or an eight-fold one on the rotation axes parallel to the [001] axis. The four-fold set is represented by positions on the intersections of the reflexion planes, on which the S atoms are already placed. This is the only four-fold set of points in the cell except symmetry centres. All the oxygens would therefore have to lie on these intersections, which is impossible with tetrahedral groups.

The eight-fold set lies on the rotation axes parallel to the [001] axis, in groups of four points about the intersections

of the reflexion planes. Oxygens in these positions could only form interpenetrating tetrahedra and would also be out of phase with the sulphur for the (020) and (002) reflexions.

Points with two degrees of freedom are confined to the reflexion planes, and each independent point forms a set of eight in the cell. If now we place a regular tetrahedron with two of its oxygens in one reflexion plane, equidistant from the other, and the two other oxygens similarly in the intersecting reflexion plane, the conditions of symmetry are fulfilled and the sixteen oxygens may be regarded as made by the operations of symmetry on two atoms, involving only two independent parameters.

This at once introduces an enormous simplification in the determination of the crystal structure. The SO_4 group as a whole has only one degree of freedom, namely movement along the axis of intersection of the reflexion planes. Its position is therefore dependent on a single parameter. The uncertainty of size of the SO_4 group introduces a second parameter, so far as intensity measurements are concerned, which may be regarded as the distance between oxygen centres in the tetrahedron.

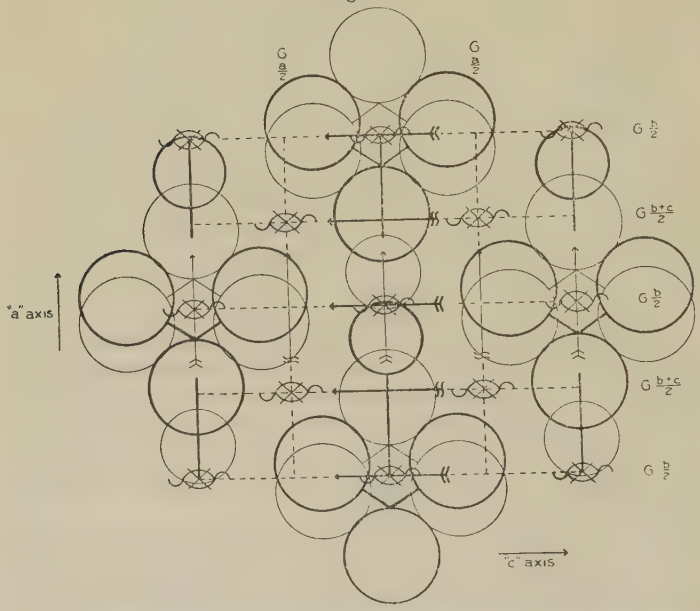
The four calcium atoms still require to have places assigned to them in the unit cell. Two possible arrangements would be to situate them all at either of the two sets of four-fold symmetry centres. Intensity considerations show that they would then be in phase with the sulphurs in the (002) and out of phase in the (020) reflexion, so that these spectra would be of unequal intensities.

The only other possible distribution of four atoms in the cell is to place them similarly to the sulphurs on the axis of intersection of the reflexion planes. Their position will therefore also be determined by a single parameter, the possible variation of which is limited by the freedom of movement of the calcium atom between consecutive SO_4 groups. If we take the known distance between calcium and oxygen centres in other crystals and assume it to have approximately the same value in anhydrite, it is clear that any displacement of the calcium from a position midway between the SO_4 groups must be small unless serious distortion of the SO_4 tetrahedron be postulated.

Once we assume the dimensions of the SO_4 group to be fixed, and the calciums limited to positions nearly midway between two SO_4 groups, the problem of determining the approximate structure reduces to that of finding a single parameter. This may be thought of as defining the displacement of two contiguous (010) sheets of atoms which slide in opposite directions along the [100] axis.

When the operations of the various glide planes are considered, we see that each sheet consists of similarly oriented tetrahedral SO_4 groups arranged on a face-centred pattern, the calcium atoms lying in a similar pattern between consecutive SO_4 groups on the same axes. This is shown by fig. 2. The orientation of SO_4 groups is reversed in alternate sheets, as can be seen in fig. 3, where the sheets are shown

Fig. 2.



The large circles represent oxygen atoms, the small ones calcium atoms. Both are shown two-thirds their relative size compared with the unit cell. Thick circles indicate groups lying $b/2$ above those shown by thin circles.

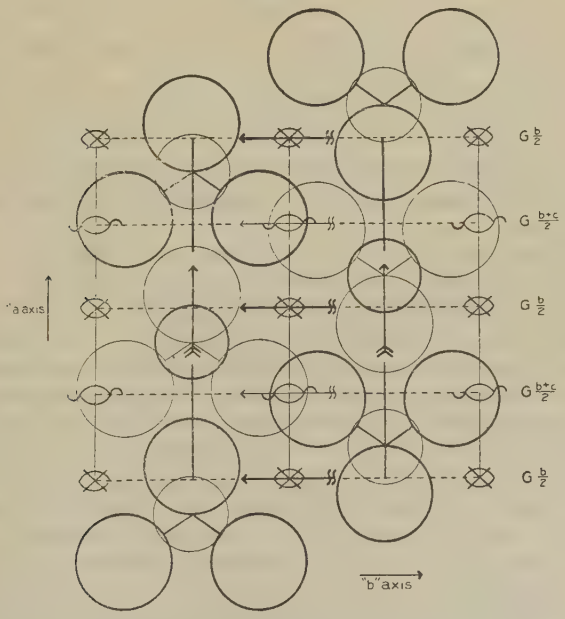
edge-on, and the manner in which they can slide in opposite directions about the symmetry centres, parallel to the [100] axis, becomes clear. A rough model, and diagrams made with the approximately known dimensions of the calcium atom and SO_4 group, showed the packing of such an arrangement in the unit cell to be feasible.

6. *Determination of Parameters.*

Figs. 2 and 3 show that for the (010) and (001) planes, all atoms except two oxygens in each $CaSO_4$ complex lie on

the X-ray reflexion planes, thus explaining the high value of the second order spectra (first observed spectra) and, since the effect of the oxygen atoms is known to fall off rapidly at higher angles, the pseudo-normal appearance of the higher orders. The interest of the reflexions from these planes lies further in the fact that the only parameter involved is the distance between oxygen centres in the SO_4 group. At first it was hoped that this would enable a comparatively accurate estimate to be made of the dimensions of the group. Owing, however, to the small percentage of the total effect contributed by the oxygens, even in the low order spectra, the calculated intensities are comparatively insensitive to variation of the parameter.

Fig. 3.



All faces in the [100] zone have intensities which depend solely on this oxygen-centre parameter, and the measured intensities from the (011) face have the additional advantage over the pinacoid reflexions that all four oxygen atoms are out of phase with the calcium and sulphur. Here also it was found that reasonable variation of the parameter gave no clear indication of its optimum value. The (022) reflexion is fairly sensitive to variation of the parameter, but again values between 2·4 and 2·5 Å seem equally satisfactory.

Table I. gives the variation in the calculated normal intensity of reflexion (ρ/S^2), for different oxygen parameters, of the various spectra from the two faces.

TABLE I.

Spectra.

Parameter Å	020	040	060	080	0.10.0	022	044	066
2·3	698	200	54·0	13	7	375	38·4	12·2
2·4	752	187	54·3	13	7	504	34·7	12·2
2·45.....	768	171	54·6	13	7	575	34·3	12·2
2·5	792	162	55·0	13	7	669	31·6	12·2
2·6	835	147	56·5	13	7	908	28·6	12·2

The distance between oxygen centres was finally taken as 2·45 Å, this giving the best concordance for all spectra considered.

The scattering power of the oxygens is so reduced in other faces of the zone by the increasing glancing angle that no conclusion can be drawn from their intensities.

Taking into account the low accuracy of the intensity measurements, it was not possible therefore to determine the distance between oxygen centres from measurements on this zone alone, without additional evidence derived from reflexions involving the two other parameters of the system.

All these parameters are most conveniently expressed, for the purpose of intensity calculations, as angular differences in phase, the dimensions of the unit cell representing phase differences of 360° in the directions of the crystal axes.

It seemed reasonable to assume as a first approximation that the calcium atoms lie half-way between two SO_4 groups, so that the two unknown parameters could not differ widely from the values $n°$ and $(n+180)°$. An important clue as to the approximate value of n is given by the strength of the (210) reflexion. This shows that the atoms must be grouped very close to these planes, and from fig. 3 this can be seen to occur when n is in the neighbourhood of $-35°$ for calcium, giving $+145°$ for sulphur, the coordinates being referred to a centre of symmetry for simplicity in calculation.

A systematic test of the assumed structure was then

carried out, and the effects of variation of both parameters investigated. The method of carrying out such tests has already been described by James and Wood (*loc. cit.*) and need only be summarized here.

All observed spectra are tabulated in order of increasing glancing angle, and the observed intensities divided by the calculated intensity ratios to give the 'normal' intensity ρ_n of reflexion that would be given by all the atoms in phase at that particular angle. If the structure is correct, ρ_n diminishes rapidly and steadily with increasing angle. Any violent anomaly indicates that the structure is incorrect, but the test must be regarded at present as principally of qualitative significance.

In assigning scattering powers at different angles to the atoms, numerical values were first taken from Hartree's tables of F values *. Oxygen and sulphur were assumed to be ionized with the charges O^{-2} and S^{+6}. We experienced difficulty, as already noted by James and Wood, in obtaining agreement with observation for the higher order spectra unless the scattering power of O^{-2} is made to die away more rapidly than given by Hartree's figures. We finally used both for oxygen and sulphur the values given by James and Wood (*loc. cit.*), Hartree's values being taken for calcium only.

A few trial intensity calculations showed that the ratio ρ/ρ_n was more nearly proportional to the square of the amplitude ratio S, which was calculated in the usual way, than to S itself, indicating that anhydrite is not to be regarded as forming perfect crystals, but a mosaic. This was checked by direct calculation from the formula for the integrated reflexion

$$\rho = \frac{N^2\lambda^3}{4\mu} \cdot \frac{e^4}{m^2c^4} \cdot \frac{1+\cos^2 2\theta}{\sin 2\theta} \cdot S^2 e^{-B\sin^2\theta} \times (\Sigma F)^2, \quad (1)$$

using for the linear absorption coefficient μ the value 25·7 derived from Wingårdh's mass absorption coefficients for molybdenum radiation †, with no allowance for extinction effect or Debye factor. Thus for the (020) spectrum (ΣF) as calculated was 41·4, while the value from Hartree's curves is 59·4. If extinction and the Debye factor were taken into account the calculated value would be raised. A normal reflexion curve for various values of $\sin\theta$ was also calculated from formula (1). The calculated values, shown in the last

* Phil. Mag. I. p. 289 (1925).

† *Zeitschr. f. Phys.* viii. p. 263 (1922).

column of Table II., agree more closely with the observed intensities than would be the case on the assumption that ρ is proportional to S.

TABLE II.

Spectrum.	Sin θ (θ=glancing angle).	$\rho \times 10^6$ $\left(\frac{E\omega}{I} \times 10^6\right)$.	$\frac{\mu+\epsilon}{\mu} \cdot \rho$.	S^2.	$\rho_n = \frac{\mu+\epsilon}{\mu} \cdot \frac{\rho}{S^2} \times 10^6$.	Theoretical value of ρ_n.
101	0·0766	?	?	0·00866	?	2450
111	0·0920	4·8	4·9	0·00296	1650	1850
002 } 020 }	0·1021	280·0	560·0	0·365	1580	1580
200	0·1143	29·0	32·0	0·0207	1550	1310
210	0·1251	170·0	279·0	0·133	2100	1080
121	0·1277	9·6	9·9	0·00232	4270	1050
022	0·1445	32·4	36·5	0·0563	647	785
202	0·1532	11·0	11·5	0·0352	327	685
220	0·1533	102·0	141·4	0·339	418	685
222	0·1841	13·4	14·1	0·0405	348	420
004 } 040 }	0·2042	90·0	121·0	0·526	230	310
400	0·2286	7·4	7·6	0·034	224	220
303	0·2298	?	?	0·0271	?	215
420	0·2502	16·0	16·9	0·274	61·7	160
402	0·2503	30·4	34·0	0·152	224	158
242	0·2554	9·0	9·3	0·0414	224	145
333	0·2760	?	?	0·0298	?	100
044	0·2890	17·8	19·0	0·524	36·3	83
006 } 060 }	0·3063	54·0	65·2	0·990	65·9	63
404	0·3064	7·4	7·7	0·345	22·3	62·5
440	0·3066	21·0	22·8	0·400	57·0	62·0
062	0·3229	27·5	30·4	0·833	36·5	50·6
600	0·3429	31·5	35·2	0·713	49·3	40·5
620	0·3676	26·0	28·6	0·723	39·5	31·6
444	0·3680	9·3	9·6	0·582	16·4	31·5
630	0·3753	?	?	0·250	?	31·0
505	0·3830	?	?	0·00203	?	28·0
363	0·3831	?	?	0·00012	?	28·0
008 } 080 }	0·4084	13·0	13·6	1·0	13·6	23·7
066	0·4335	12·2	12·7	1·0	12·7	20·6
800	0·4572	0·2	0·2	0·0298	6·7	18·4
606	0·4596	8·1	8·4	0·750	11·2	18·2
660	0·4599	12·0	12·5	0·752	16·6	18·2
555	0·4600	?	?	0·00007	?	18·2
840	0·5004	?	?	0·0302	?	16·1
804	0·5006	?	?	0·031	?	14·9
0.0.10 } 0.10.0 }	0·5105	7·0	7·2	1·0	7·2	14·0
484	0·5108	5·6	5·7	0·590	9·5	14·0
666	0·5520	2·4	2·4	0·745	3·2	11·4
10.0.0	0·5715	0·3	0·3	0·97	0·3	10·4

The intensities ρ of all observed spectra were expressed in absolute measure, taking the absolute intensity of reflexion from (400) rock-salt as 10^{-4}. ρ/S^2 gave then the value of ρ_n. Allowance for the unequal effect of extinction, which cuts down the more intense reflexions to a disproportionately large extent, was made by putting $I \propto S^2/(\mu+\epsilon)$, where the extinction factor ϵ is proportional to the intensity of reflexion I and can be written $\epsilon = \alpha I$ *. The value of α for anhydrite was deduced from the ratio of the calculated normal intensity (derived from the measured (020) intensity) to the normal intensity calculated theoretically from formula (1). All observed intensities were then multiplied by the factor $(\mu+\epsilon)/\mu$ to correct for extinction. These corrected values, divided by S^2, should form a steadily diminishing series corresponding to the theoretical intensity values, but still affected by neglect of the Debye factor.

Table II. shows our results in this form.

The parameters which gave the best agreement were calcium $-35°$ and sulphur $+145°$. These values represent displacements along the a-axis of $-0{\cdot}60$ and $+2{\cdot}50$ Å respectively. The degree of accuracy with which the parameters could be fixed is of the order of $\pm 0{\cdot}05$ Å. The calcium atoms appear then to be half-way between consecutive SO_4 groups on the a-axis, and adjacent sheets of atoms parallel to the (010) face are displaced 1·21 Å with respect to each other.

7. *Discussion of Results.*

Five of the forty-five spectra examined show considerable discrepancies in the series. These are the (101), (210), (121), (420), (630) reflexions.

From the calculated amplitude factor we should expect the (101) reflexion to have an intensity of about 20 per cent. that of (400) rock-salt, whereas its presence could not be detected at all. Moreover, this discrepancy cannot be satisfactorily overcome by any reasonable alteration in the parameters. Now the amplitude factor is quite sensitive to change in the F value for sulphur. The glancing angle is the lowest observed, and it is precisely in this region that the F value is most uncertain, and changing at its greatest rate. It would seem, at first sight, logically correct to adopt Hartree's curve for S^{+6} throughout the series. Thus, for the (101) reflexion, F would have the value 10, instead of the value 14·2 taken by us from James and Wood, and

* *Cf.* W. L. Bragg, Phil. Mag. l. p. 309 (1925).

the resulting amplitude factor would be reduced from 0·0087 to 0·0024. But this change adversely affects the four or five spectra occurring at angles where the divergence of the F curves for S^{-2} and S^{+6} is still appreciable. The (111) and (121) spectra are especially sensitive to the change, the calculated normal reflexion for the latter assuming such a value as to render the change questionable.

Some polarization of the oxygen atoms of the SO_4 group seems likely, and it is possible that the intensity at low glancing angles is affected by the asymmetry of the oxygen electron shells.

However, we have been unable to reach a satisfactory compromise, and have preferred to retain the F values that give concordant results in other structures.

The (121) reflexion gives too high a value for ρ_n, but the low observed intensity and the sensitivity of the very small amplitude factor could easily account for this.

The three remaining discrepancies occur in reflexions of different orders from the (210) planes. As already noted, the calcium and sulphur atoms are closely concentrated near these planes, and the combined scattering power of all oxygen atoms is only one-fifth of the total effect, even in the first order. The contribution of the oxygens is, however, quite susceptible to variation in the sulphur parameter. It is in faces of this character also that small distortions of the SO_4 tetrahedra might be expected to produce considerable effect.

The coordinates already chosen appear to give the best general agreement when all spectra are considered.

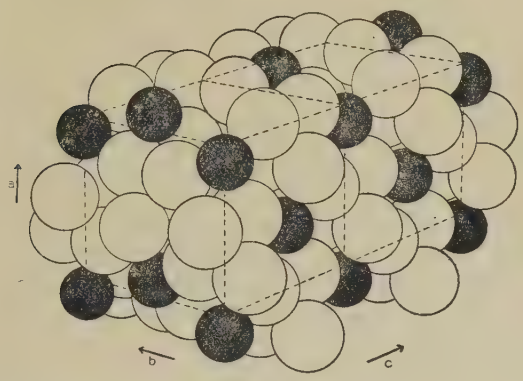
Fig. 4 shows the structure to scale, the black spheres representing calcium ions, and the white spheres oxygen ions grouped in tetrahedra; the sulphur ions not being visible. The positions of two contiguous unit cells are indicated by dotted lines.

The *b* face of the model reveals the face-centred arrangement of the calcium atoms and SO_4 groups, whereas the *c* face shows the displacement of alternate sheets of atoms in the *a* direction.

Each calcium atom is immediately surrounded by eight oxygen atoms belonging to six tetrahedra, four of these being at a distance of 2·55 Å; two at 2·43 Å, and two at 2·47 Å. The nearest distance of approach of calcium to oxygen has been found in other crystals to be 2·4 Å. It is clear, therefore, that the calcium atoms are surrounded as

uniformly as possible by oxygen atoms, the arrangement of the oxygens in tetrahedra preventing perfect uniformity.

Fig. 4.



The smallest distance between calcium atom centres is 3·68 Å ; the distance between sulphur and oxygen centres is 1·50 Å.

Summary.

The structure of anhydrite has been determined by the ionization spectrometer. It is based on a simple orthorhombic lattice, the unit cell containing four molecules. The space-group V_h^{17} previously determined by Rinne, was corroborated by the Debye powder method.

Assuming a regular tetrahedral arrangement of the SO_4 group, two parameters suffice to fix the positions of all its atoms in the unit cell. The positions of the calcium atoms involve only a single parameter.

In calculating amplitude factors, some deviations from Hartree's F values for scattering power have had to be made, as already noted by other workers.

We wish to express our thanks to Professor W. L. Bragg, F.R.S., for his help and interest in the progress of the work. We are also indebted to Mr. R. W. James for much helpful advice and criticism.

Note.

Since writing this paper we have seen a copy of a most interesting determination of the structure of anhydrite and

the configuration of the SO_4 group by J. A. Wasastjerna *, communicated to the Societas Scientiarum Fennica on Sept. 23rd, 1925.

The author shows from symmetry and intensity considerations that a tetrahedral arrangement of the SO_4 group is the only possible one, and deduces a structure from which ours differs only in the values of the parameters.

But in the theoretical calculation of reflexion intensities he states that, on empirical grounds, he considers it impossible to obtain agreement between observed and calculated intensities for anhydrite if the intensity is taken as proportional to the square of the amplitude factor (S^2), whereas he was able to get a fairly good agreement by taking the intensity as proportional to S ; that is to say, treating anhydrite as an approximately perfect crystal. As shown in our paper, this does not seem to be justifiable either on a theoreticl or empirical grounds.

In calculating reflexion intensities Wasastjerna uses the formula

$$R = \frac{1}{\sin^2\theta}\Sigma\rho_m \cos 2\pi n(hx_m + ky_m + lz_m),$$

and treats the scattering power ρ_m of an atom at various glancing angles as approximately constant.

With the exception of the pinacoid reflexions, which were measured spectrometrically, his observed intensities are taken from powder photographs using copper radiation, and are merely classified into five degrees from "very strong" to "very weak."

It is interesting to note that he obtains a weak (101) reflexion.

In terms of our notation his coordinates become Ca $= -54°{\cdot}0$ S $= +126°{\cdot}0$, in place of our Ca $= -35°$ S $= +145°$.

The mean distance between oxygen centres in the SO_4 tetrahedron is 2·7 Å as against our value 2·45 Å.

Manchester University.
12th March, 1926.

* *Soc. Scient. Fenn. Comm. Phys.-Math.* ii. p. 26.

IX. *A New Method of obtaining a Luminous Discharge in Gases at very Low Pressures.* *By* E. W. B. Gill, *M.A., B.Sc., Fellow of Merton College, Oxford, and* R. H. Donaldson, *M.A., University College, Oxford* *.

(1) THE discharges in gases at low pressures obtained with alternating potentials or with high-frequency potentials, such as are obtained in ordinary oscillatory circuits, have been the subject of many investigations, but no measurements appear to have been made of the potentials required to maintain currents in gases when the frequency of the oscillatory potential is of the order of 40 million oscillations per second, which is the frequency corresponding to a wave-length of about 8 metres.

We have recently made some investigations of the currents in gases with potentials differing in frequency over a very wide range, and we find that the absolute value of the potential required to maintain a current in a gas is greatly reduced when oscillations of very short wave-lengths are used. It is difficult to measure these potentials accurately, but the effect of increasing the frequency is so marked that it is sufficient in this preliminary account of the experiments to give the values of the potentials to an accuracy of about ten per cent.

To illustrate this effect we give the results of experiments made with hydrogen, where the potentials required to maintain a small current at different pressures were determined, (*a*) with direct voltage, (*b*) with voltages alternating about 200,000 times a second, and (*c*) with voltages alternating about 40,000,000 times a second. The last investigation revealed a simple method of obtaining a luminous discharge through a gas at a pressure of a thousandth of a millimetre of mercury, that is at a pressure considerably lower than that in an ordinary X-ray tube.

(2) The discharge-tube used was a glass cylinder about 25 cm. long and 4·5 cm. diameter. The electrodes were two brass rods of diameter 1 mm.; they were sealed into two side tubes through copper glass seals, and these side tubes were sealed into the main tube not quite opposite to each other in such a way that the brass rods were parallel and about 3 cm. apart. The actual shape of the tube is shown

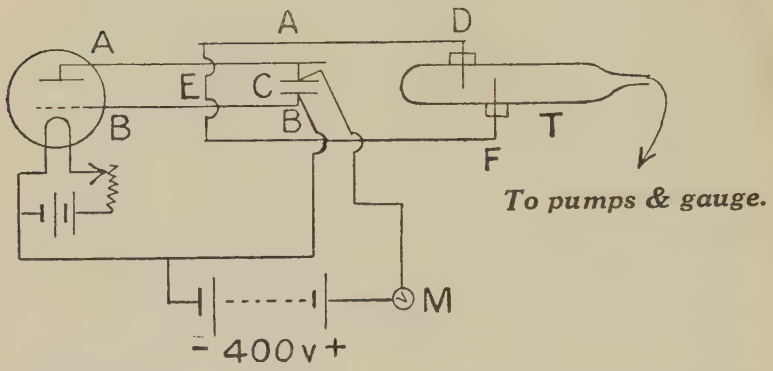
* Communicated by Prof. J. S. Townsend, M.A., F.R.S.

in fig. 1, where D and F are the two rods projecting into the main tube T.

The tube was joined up to a mercury pump. A McLeod gauge and drying tubes and a palladium tube were also inserted.

The whole apparatus was pumped out and washed out several times with hydrogen admitted through the palladium tube.

Fig. 1.



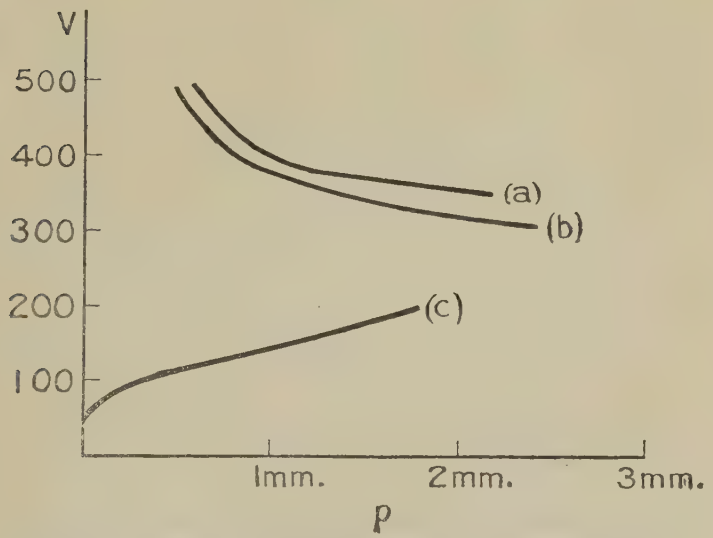
(3) The experiments to find the potentials required to maintain a small direct current through the hydrogen at various low pressures need not be described in much detail. The tube was connected to a battery of small accumulators, the current being kept as small as desired by inserting in one of the leads a small rectifying valve which would only pass a small current dependent on the temperature of the filament. The potential across the tube was read by an electrostatic voltmeter.

The results obtained are given in curve (*a*) fig. 2. The usual type of curve for maintenance potentials is one in which for high pressures the potential is very high ; as the pressure is reduced, the potential also falls and reaches a minimum, and a further reduction in pressure causes the potential to rise very rapidly. It will be seen that the range of pressures worked over in curve (*a*) are below the pressure which gives the minimum potential.

(4) The next set of experiments, curve (*b*) fig. 2, were done with an alternating E.M.F. An oscillatory circuit consisting of an inductance and capacity was maintained in oscillation by a valve using the ordinary reaction circuit. The wave-length of the circuit was 1430 metres, corresponding to a

frequency of 210,000 alternations per second. The discharge-tube and the electrostatic voltmeter were both connected across the condenser. When the valve (a Mullard 0 30 A) was taking its rated filament current and 400 volts in the plate circuit, there was enough potential across the condenser to light the discharge-tube brightly at pressures of a few millimetres of mercury. The strength of the oscillations was then reduced by gradually reducing the filament current of the valve till the discharge was only just maintained.

Fig. 2.



Minimum potential V required to maintain a discharge at different pressures *p*.

(*a*) Direct current. (*b*) Current periodicity 200,000.
(*c*) Current periodicity 40,000,000.

The potentials indicated by the electrostatic voltmeter as being necessary to maintain the discharge are shown in curve (*b*). It should be noted that these potentials are not the maximum potentials across the tube as the voltmeter gives the mean square of the potential. The maximum, or "peak" value, would be obtained by multiplying the readings by $\sqrt{2}$, though this would not be quite accurate as the wave-form was not exactly that of a sine curve. The general shapes of the two curves (*a*) and (*b*) are much the same.

(5) The last set of experiments given by curve (*c*) fig. 2

was made with a much higher frequency, a wave-length of 8·25 metres being used corresponding to about $3{\cdot}6 \times 10^7$ alternations a second.

The short-wave generator was a slight modification of the type devised by Townsend and Morrell*, and is shown in fig. 1.

AA and BB are two brass strips 13 mm. by 3 mm., each 161 cm. long, placed flat and parallel to each other, the distance between their centres being 6·5 cm. One end of AA is joined to the plate of a Mullard 0 30 A valve and one end of BB to the grid. The other ends of the strips are joined to the condenser C, which is of the order of a milli-microfarad. The plate is charged to about 400 volts positively to the filament by a lead brought into AA at the condenser end, and the grid is put at the same potential as the negative end of the filament by a similar lead to BB. It was convenient to have a milliammeter M in the plate lead.

When the valve filament is heated by a six-volt battery this set produces powerful oscillations with a wave-length of 8·25 metres. The presence of these oscillations is shown by the milliammeter M reading from 40 to 60 milliamps, whereas if the oscillations are damped by touching BB at the grid end the plate current drops to a few milliamps.

The amplitude of the oscillating current is not the same everywhere along the strips, being largest at the condenser end and smallest at the grid end.

This arrangement is so simple and convenient for short waves that a few more remarks may be of assistance. AA and BB need not be strips, ordinary wire or rod will do, and their distance apart is not important except that it should not be less than 3 or 4 cm. The size of the condenser C is not important either, provided it is not too small it will be situated at a potential node and have no effect on the wave-length. It should be noticed that it has a potential of 400 volts across it.

Any small transmitting valve dissipating about 30 watts at the plate will be suitable, but the wave-length will vary slightly with different valves. The leads from the H.T. battery and filament to the condenser ends of AA and BB should not lie too close to the strips.

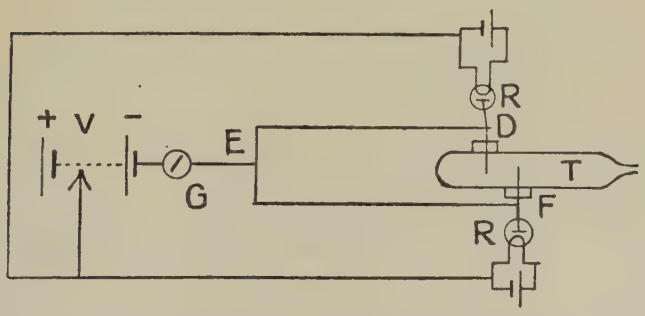
As mentioned above, with strips 161 cm. long the wave-length was 8·25 metres. A rough rule is that a reduction x in the length of the strips reduces the wave-length by $4x$, so that the length of strip for any desired wave-length λ is $\frac{\lambda - 181}{4}$ cm., λ being measured in cms. The oscillations are not very powerful for wave-lengths less than 3 metres.

* Phil. Mag. August 1921.

It is not possible to put the discharge-tube directly across the oscillating system as the potential differences are scarcely large enough, and in addition the 400 volts steady potential would be superimposed upon the alternating potential. A further objection is that the capacity of the discharge-tube and the current through it would disturb the wave-length.

The tube therefore was put across a circuit DEF electromagnetically coupled to the oscillator. This circuit has a natural wave-length of about 4 times the length DE, and when it oscillates E is a potential node and the maximum potential occurs between the free ends, *i.e.* across the discharge-tube. It is not necessary to tune this circuit accurately to the wave-length of the transmitter, as sharp resonance effects are not obtained when a discharge occurs in the tube T, but it is desirable to make the length DE somewhere about $\lambda/4$. In our experiments this length was about 2 metres, and a convenient coupling was obtained when the two circuits overlapped by 60 cm., the plane of the circuit DEF being about 3 cm. above the plane AABB. If the coupling is too tight the wave-length of the transmitter will be altered, or in extreme cases the valve may not be able to produce oscillations.

Fig. 3.



The measurements of the oscillating potential across the discharge-tube presents very considerable difficulties, and the method to be described does not claim to be more than a rough one though sufficient for our purposes, as we only desired to know the general shape of the curve.

It is not possible to attach to the ends D, F any measuring device which has a capacity of more than a few electrostatic units, as the potential would be too much reduced thereby, and the method therefore finally adopted is shown in fig. 3. R, R are two small rectifying valves whose plates

are joined to the secondary circuit at the same points as the discharge-tube. The negative ends of the filament batteries of these valves are joined back to the point E through a variable source of potential V and a delicate galvanometer G.

The point E is a node of potential, and if its potential is taken as zero the potential of D will be $V_0 \sin pt$ when that of F is $-V_0 \sin pt$. If V is greater than V_0 the plates of the rectifying valves must always be at a negative potential relative to their filaments, and no current can flow through the valves. If V is less than V_0 the plates are positive to the filaments once in each alternation, and currents will flow through the valves and be registered by G.

V is therefore adjusted till G just reads no current, and the value of V_0 thus found. The "peak" value of the alternating E.M.F. is $2V_0$.

Were it not for the valve capacity one valve would be sufficient, two similar valves keeps the set symmetrical.

This arrangement as already stated is not ideal. The potential measured is that just outside the discharge-tube, which is not quite the same as that between the electrodes where the discharge is occurring. There may be a small potential distribution down the leads from the filaments to E, and for the high frequency used the time the electrons take to cross the valves is for small voltages comparable to the time of oscillation, which will introduce an error not yet estimated but not more than a few volts. The method of experiment was to have the transmitter and secondary circuit coupled together, the secondary circuit having its two rectifying valve circuits attached, and the transmitting valve was then turned full on. If the tube did not light up it could generally be started by a spark from a small induction coil, one of the secondary terminals of which was joined to the node E and the other of which was placed about 1 cm. from the wire at F. The discharge was then reduced either by loosening the coupling, or reducing the filament current of the transmitting valve, or both, till the discharge was only just passing, when the peak voltage $2V_0$ was determined as above. The results for various low pressures are shown in curve (*c*) fig. 2.

For very low pressures the only way to get the discharge going was to raise the pressure slightly, start the discharge, and then, keeping the discharge running, pump down again to the lower pressure. When the discharge was going it was not possible to stop it by reducing the pressure as far as it could possibly be reduced by a Toepler pump.

(6) Curve (*c*) shows that there is a very striking difference between the conditions for the maintenance of a discharge when the applied E.M.F. alternates 36 million times a second and when it alternates 200 thousand times or is unidirectional. In the latter cases, the minimum potential for maintenance with the tube used occurs at about 3 mm. pressure, but in the former case, even when the pressure had been reduced to 1/50 mm., the minimum potential had not been reached. The difference in the magnitude of the potentials required is also remarkable; the R.M.S. of the minimum potential for the 200 thousand oscillation is about 300 volts, but with the 36 million oscillation a peak valve of 100 volts will maintain the current with pressures much smaller than that at which the ordinary minimum sparking potential is obtained.

The large effect obtained with the short-waved oscillations may be seen from the consideration that the pressure of 1/100 mm. of mercury is of the order of pressure of an X-ray bulb, and at about this pressure a discharge from an induction coil passed more easily through air at atmospheric pressure between electrodes 10 centimetres apart, in parallel with the bulb. Yet on the short wave at this pressure the tube was brightly illuminated, when the potential difference between the terminals was about 150 volts.

(7) The discharge in the bulb was obtained with pressure much less than 1/100 mm. It was found that if the discharge was left running with the gas at about 1/100 mm. pressure, the hydrogen gradually disappeared and the pressure fell till it was less than 1/1000 mm. At this very low pressure the spectrum of the discharge showed very bright mercury lines and scarcely any trace of the hydrogen spectrum. For this reason too much stress should not be laid on the actual values of the potential for current maintenance at the lowest pressures, as at these the mercury vapour appears to have more effect than the hydrogen.

It is worthy of note that at the very lowest pressure attained the potential required to maintain the discharge was only a few volts.

It was also found that the discharge was obtained at very low pressures in hydrogen from which the mercury vapour was removed by charcoal cooled with liquid air.

(8) From the spectroscopic point of view, the short-wave transmitter appears to offer the means of working at pressures considerably lower than those which hitherto have been found practicable. It is an advantage for spectroscopy to eliminate the electrodes, and some experiments were made

to see if the short wave would produce an electrodeless discharge. For this purpose the same transmitter and coupled circuits were used, except that the open ends of the secondary circuit, instead of being joined to the electrodes of the discharge-tube, were laid along the outside of the tube on opposite sides of it, or better still looped round it a few cms. apart. On starting the valve transmitter, it was found that the tube, if at a fairly low pressure, lit up at once. For the very low pressures it was necessary to help the discharge to start with an induction coil applied just as before described (one terminal joined to the potential node on the secondary circuit and the other a centimetre or two from one of the free ends). In this way the discharge could be started with the pressure as low as 1/500 mm. Generally speaking, it was easier to get the electrodeless discharge to pass than the discharge between electrodes. It need scarcely be added that if the luminous discharge alone is required it is unnecessary to have the two rectifying valves attached to the secondary circuit.

(9) The difficulty of obtaining the supply of electrons to maintain a direct current at very low pressures is that the majority of the electrons have very few collisions with gas molecules, and the general explanation of the ability of very rapidly alternating E.M.F.s to maintain a discharge at very low pressures is that in moving between the electrodes a large number of the electrons cover a distance many times greater than the distance between the electrodes, and thus the chance of a collision is very much larger than if the electrons passed straight across.

The general motion of the electrons up to the time they have a collision is a movement through a distance d in one direction followed by a movement d' in the reverse direction, this process being repeated indefinitely till an electrode is reached.

If the E.M.F. is V sin pt it is easy to see that in the cases where the velocity of the electrons happens to be zero at time $t = \frac{\pi}{2p}$, the electrons oscillate about a mean position; and in cases where the velocity is zero at time $t=0$ the electrons move across the tube with alternate accelerations and retardations without any reversal in the direction of motion. (These are the extreme cases.) The electrons whose velocity happens to be zero at times near to $\frac{\pi}{2p}$ have d' very nearly equal to d. These in one alternation cover a total

distance $d+d'$, but actually only approach the electrode by the small distance $d-d'$.

It is, of course, essential that in its excursion d the electron does not encounter the electrode, which agrees with the fact that the low pressure phenomena only come into prominence for the extremely high frequencies where the distances d and d' can be proved to be much less than the distance between the electrodes for the particular electric forces which produce the discharges.

(10) It would appear from the preceding argument that the discharge might prefer a low voltage to a high one as the excursions would be smaller, and it was found possible to show this experimentally. A tube was taken 95 cm. long (in this case containing air) and the pressure brought very low by the use of charcoal and liquid air. The wires of the secondary circuit were laid alongside the tube and the whole tube lit up; but by reducing the strength of the valve oscillator it was possible to light up only a portion of the tube; not near the ends of the wires where the potential was biggest, but at points where the potential was less.

These experiments were conducted in the laboratory of Prof. Townsend, who has given us very much help and advice.

X. *Shape of Waves from Large Explosions.*

By T. Carlton Sutton, *M.Sc., F.Inst. P.**

Foreword.

The following consists of:—

(1) Some deductions as to the nature of waves emitted from large explosions, based on the accepted theory of Rankins, Hugoniot, and others.

(2) The application of these deductions to registrations of the recent explosion at La Courtine, especially to a photograph taken by M. Dufour†.

In the argument that follows, the deductions (1) and their application (2) have, for the sake of interest, been developed together. The former hold good as deductions from general theory; on the other hand, although it seems appropriate and reasonable to apply them to M. Dufour's observations in

* Communicated by the Author.

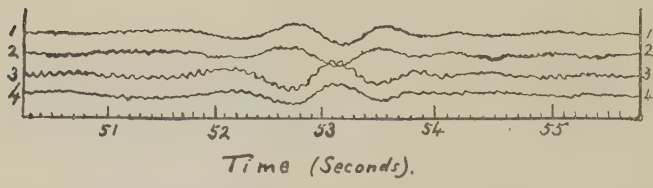
† Dufour, *C. R.*, 1924.

the way that is here done, a full justification of any such step must necessarily await the collection of further evidence of a kind that can only be obtained by experiments on a very large scale.

M. Dufour's Photographs.

SOME interesting photographs have been taken by M. Dufour at the École Normale Supérieure, and give some indication of the nature of "heavy" sound waves transmitted over a long distance. The source of these waves was the explosion of a charge of 10,000 kilogrammes at La Courtine in Central France. The waves travelled about 180 miles, and were recorded at Paris by a number of Dufour microphones. These microphones consist of a large circular disk about 1 foot in diameter, carrying at the centre a small coil; when the sound impulse is received, the disks vibrate and move this coil in an intense magnetic field. In these particular measurements four microphones were used, connected with the strings of an Einthoven galvanometer in such a way that the currents passed in one direction through strings 1 and 2, and in the reverse direction through strings 3 and 4. M. Dufour's photograph

Fig. 1.



is reproduced in fig. 1. The natural period of the microphone disks is of the order of 0·07 second, and is seen in the smaller fluctuations recorded; the larger fluctuations of approximately 1·0 second period are attributable to the explosion at La Courtine.

Deductions from General Theory.

M. Dufour's photograph was taken at Paris. On account of the distance (180 miles) from La Courtine, where the explosion took place, and since the nature of the ground, the cloud distribution etc., is not regular, the fluctuations registered may be due to irregular reflexion and refraction, and may represent the "drawing out" of a single wave-front.

Without considerably more evidence and measurement it is not possible to speak with any certainty ; nevertheless, it is of interest to examine what shape of wave-front would be expected from a large explosion, and examination may well be made in accordance with current theory *.

This theory may be developed to show that, when explosions are sufficiently large, (1) the disturbance is of a fluctuating nature, (2) its component pulses occur in groups, separated by intervals in which no pulses occur, and (3) the number and duration of these groups increase with the size of the explosion.

That portion of the theory which affects the present issue has been summarized † :—

"When in a fluid medium, a discontinuity exists of such a nature that the pressure and density are much greater on one side of it than they are on the other side, a pulse or a series of pulses is set up which tends to decrease this difference. These pulses are pressure pulses passing from the region of high pressure into the region of low pressure, through which they will continue to travel until some other surface of discontinuity is reached or their energy becomes absorbed in the medium. They travel with a velocity greater than the velocity of the particles in the medium by an amount which is commensurate with the velocity of sound in the medium, and so of course approach and reach the boundary of the medium.

"No pulses of rarefaction originate at the discontinuity."

Consider now some phenomena of the expansion in free air of a relatively large gaseous mass produced by an explosion, taking for simplicity the hypothetical case in which the explosion is imagined instantaneous throughout the mass.

The diagrams I. to IX. (fig. 2) indicate the density distribution within the explosion gases at successive instants.

a, *b*, *c*, *d*, *e*, *f*, *g*, ... *o* represent a row of actual particles extending from the outermost layer of explosion products to the centre of the explosion. Of these, *a* at the outer edge moves outward rapidly ; *b*, *c*, *d*, etc., move less rapidly ; and *o* at the centre remains stationary. Consequently, the position in space of *a*, *b*, *c*, etc., varies from diagram to diagram, but the ordinate at *a*, compared with the ordinates at

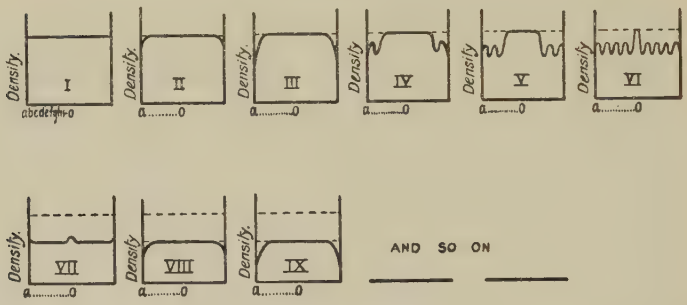
* Earnshaw, Phil. Trans. 1860. Rankin, Phil. Trans. 1870. Hugoniot, *J. de L'École Polytechnique*, 1887, 1889. Jouguet, *J. de Math. Pures et Appliqués*, 1906. Rayleigh, P. R. S. 1910. Crussard, '*La Technique Moderne*,' 1914, 1920, *et sqq.* Becker, *Z. f. Elec. Chem.* 1917.

† Jouguet, *ibid.*

b, *c*, *d*, etc., represents in each diagram the instantaneous density of the medium in the immediate neighbourhood of particle *a*, as compared with that in the immediate neighbourhood of particles *b*, *c*, *d*, etc.

Diagram I. represents the condition at, or immediately after, the explosion. In the case under consideration, conditions are then uniform for an instant, *i. e.*, pressure, temperature, density, etc., are the same throughout the exploded mass ; the gradient in the interior is zero, that at the bounding surface infinite.

Fig. 2.



When conditions are as in diagram I., particles in the outer layers immediately begin to travel outwards from the centre, driving back surrounding air and mixing with it. These outer layers are the first to expand and mix, and are therefore the first to decrease in density and pressure. Towards the centre, on the other hand, the decrease is much less rapid, because (*a*) the pressure gradient, and so the outward driving force, is less in the earlier stages of the expansion, (*b*) mixing with outside air does not occur, and (*c*) loss of energy by radiation is less. That is to say, a large and increasing drop in density takes place within the medium but in its outer layers ; the density of the inner layers remains high in comparison. This is indicated in diagrams II. and III.

Consequently, in addition to the discontinuity at the outer surface, steep density-gradients tend to form within the medium, and increase in steepness until something approaching a second discontinuity is attained.

Such gradients (continuous although steep) have not, as yet, yielded to mathematical analysis. The steeper the gradient, however, the more nearly it resembles the fully

analysed case of a "discontinuous bounding surface of infinite gradient." If (and when) the gradient in this critical steep region becomes sufficient, a pressure pulse * is formed and passes outward through the explosion gases towards the bounding surfaces and the regions of lower pressure (diagram IV.).

The gradient is thus relieved, so that the neighbouring region towards the centre becomes the region of maximum gradient.

As the expansion continues, the gradients further increase, and a second pulse originates a finite distance within the bounding layer (diagram V.).

Similarly, subsequent pulses originate further and further from the boundary, the position of the successive surfaces at which they form passing towards the centre. Diagrams IV. to VI. indicate these phases of the pressure-distribution.

In general, this formation of pulses continues until the converging spherical surfaces of formation extend to the original centre of explosion, where they contract to a point. In this respect the pressure distribution has become that shown in diagram VI. The energy of the central region of higher pressure has now been expended, and the production of pulses ceases. As the last pulses pass outwards the distribution in diagram VII. is attained.

When relatively small masses of explosives are detonated, substantially the whole of the energy of detonation has been dissipated by the time this stage is reached.

If, however, sufficient energy remains, the conditions in diagram VII. are similar to those in diagram I., and are favourable to the production of a further series of pressure-pulses in the medium. If the size of the explosion is sufficiently large, phases II. to VI. may therefore be repeated time after time and series after series of pulses be formed.

Within the mass of explosion products, therefore, there may originate a number of series of pressure-pulses passing outwards, separated by periods during which no such pulses pass.†

Whenever a new series of pulses reaches the expanding boundary between products and air, the fall of pressure at the bounding surface is momentarily checked (may even

* Such pulses are additional to any which are formed at that "outer" discontinuity which necessarily exists where the outermost layer of the explosion gases is pressing against the external air.

† In explosions of small or of moderate size, only one such series forms. In larger explosions, several series may form.

be converted momentarily into a rise). The pressure between products and air therefore fluctuates in period with the arrival of each series of pulses.

In a sufficiently large explosion, therefore, the wave impressed upon the outside air is also fluctuating. It consists of a main pressure-pulse and a number of smaller superimposed pulses which themselves occur in groups and are related to the several series of pulses discussed above.

The size, period, and general nature of each such series depend on the conditions of the explosion products at the time of origin of the series. Such relation as may exist between the periods of the various series will not be a simple one, and it would be better to use observations of these periods to determine the condition of the explosion products, rather than to argue in the reverse order.

Application to M. Dufour's Photograph.

The e.m.f. induced in a magnetic coil attached to a drum diaphragm, such as was used by M. Dufour, records directly the rate of increase or decrease in pressure of the superincumbent air. A fluctuating series of groups of pulses causes, therefore, a record in which the trace passes alternately above and below the zero position, according as the pressure is momentarily increasing or decreasing.

M. Dufour's photograph is of this nature.

The simple theory developed above cannot rightly be applied unless the explosion occurs (1) in free air, and (2) at the same instant throughout the whole mass. Neither of these conditions applies to the explosion at La Courtine. The full theory will necessarily be more complex. This theory will, however, involve the production of series of pulses as in the case of the simple theory, and the chief features of M. Dufour's photograph may perhaps be interpreted on these lines rather than as the result of a mere "drawing out" of a single wave-front by refraction and by reflexions from earth and clouds. If this can be done, it would follow that :—

(i.) The groups of pulses received at Paris were of recordable magnitude for at least five seconds and were of a composite nature.

(ii.) During this time the disturbance travelled at least one mile ; the wave-front, therefore, was at least one mile in thickness.

(iii.) The gradients within the expanding explosion gases, and between them and the surrounding air, were appreciable for five seconds.

(iv.) At least five series of pressure-pulses were formed in the explosion gases during this time.

(v.) The time between the passage of the first and that of the second series of pulses (1·5 secs.) was considerably greater than the time between the passages of subsequent series (less than 1·0 sec.).

(vi.) The rate of change of pressure on the microphones (*i.e.* the suddenness with which pulses were produced in the explosion gases) was greatest for the second and third series.

Variation with Size of Explosion.

The time occupied in the formation of a series of pulses in the way described above, depends upon the time taken by the converging spherical surfaces (of steep gradient) to pass to the centre of explosion. In general, the greater the volume of explosive detonated the longer the path to be traversed by these surfaces, and consequently the longer the recorded pulses.

M. Villard * and M. Dufour have noted this from the experimental side. By examining a large number of sound-ranging records they have traced this relation between "size of gun and duration of the wave emitted" (measured by the time during which the strings of an Einthoven galvanometer remain deflected), and found that the duration of the wave increased with the mass of explosive fired. The prolonged deflexions in the case of the explosion of 10,000 kilogrammes at La Courtine confirms this relation.

A more detailed analysis of this matter is scarcely warranted at present; these remarks are confined, therefore, to indicating how this interesting and remarkable record may be interpreted in accordance with the demands of current theory.

My thanks are due to the Director of Artillery for authority to publish.

Research Department,
Woolwich.

* Villard, *Comptes Rendus*, 1924.

XI. *The Transmission of Sound through the Head.* By H. Banister, *B.Sc.* (*Lond.*), *Ph.D.* (*Cantab.*), *St. John's College, Cambridge* *.

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I. Introduction.

1. THE transmission of sound from one ear to the other through the head has long been a matter of interest to scientists. Not only is it important from the point of view of the general theory of hearing, but also many investigators have suggested that transmission, by way of the bones of the head, is a factor which assists in the localization of sounds.

2. In spite of its importance very little experimental work appears to have been done on the problem, neither, so far as I know, has it ever been clearly formulated.

3. A similar problem has confronted architects and builders, who have been called upon to construct sound-proof rooms; and it is only recently, chiefly within the

* Communicated by the Author. This research was carried out in the Psychological Laboratory, Cambridge, with the aid of a grant from the Medical Research Council.

last ten years, according to Watson * that the question of the transmission of sounds through buildings has been scientifically investigated.

4. In his monograph on "Sound Proof Partitions" Watson points out that two types of transmission must be discriminated. In the first type the sounding body is directly in contact with the framework of the building: in the second it is not. With the former the building itself is put into vibration, and the sounds are conducted to great distances; with the latter the sounding body sets up vibration *in the air* of the room in which it is situated. These aerial vibrations travel to the boundaries of the room, and may be transmitted to the other side through the partitions.

5. Transmission of the second type (aerial sound-waves) may take place, Watson maintains, in three ways:—(*a*) Firstly, through narrow cracks or holes, which form continuous air channels, along which the waves can percolate to the other side. This is the most common form of transmission. Sound-waves can, in this way, pass through considerable thicknesses of hair, felt, and flannel. (*b*) Secondly, the aerial waves may set the partition, or some part of it, into vibration. The partition then transmits the vibrations to the other side, setting up sound-waves on the further side as a telephone diaphragm might. With ordinary rigid walls such transmission is very slight. (*c*) Thirdly, the aerial waves may arouse elastic waves in the solid structures of the partition—waves of the same nature as those set up in the framework of the building when the vibrating body is itself in contact with the framework. The amount of this transmission is practically infinitesimal, not because the walls will not transmit such sound-waves, but because of the great difficulty in initiating them. Aerial sound-waves, even of great loudness, have comparatively little energy. The amplitude of the aerial vibration of a loud sound is, according to Shaw †, of the order of ·004 in. So that it would be surprising if the light air particles, vibrating with so small an amplitude, had any appreciable effect on the heavy, rigidly held, particles of a wall.

6. As with buildings, so also when considering the transmission of sound energy through the head, we must clearly

* Univ. of Illinois; Eng. Expt. Station Bull. No. 127, pp. 1–78 (1922); Engineering, 114, pp. 196–197 (1922).

† Proc. Roy. Soc. A, lxxvi. pp. 360–366 (1905).

discriminate between (*a*) vibrations set up in the framework, the bones, etc., by direct contact with the sounding body, and transmitted to the ears by what may properly be termed "Bone-conduction"; and (*b*) vibrations due to the arrival of aerial sound-waves at the ears. It is with the latter type of transmission that we have to deal. With the former we have little concern in ordinary life, since sounds usually reach our ears as aerial waves.

7. Aerial sound-waves, falling on one ear in the usual manner through the meatus, may conceivably be transmitted through the head so as to affect the other ear in three ways:—

(*a*) The vibrating tympanum may set the air in the middle ear at the near side into vibration, and these aerial waves may pass through the sinuses or air passages to the far ear.

(*b*) The head may be made to vibrate as though it were a diaphragm, *cf.* para. 5 (*b*), when the far tympanum, in contact with the relatively stationary air on that side, would be set into motion.

(*c*) Elastic waves may be set up in the framework of the head and thus transmitted to the far ear.

It seems probable, however, that any transmission which may occur, with sounds of ordinary intensity, is due either to (*a*) air transmission through the sinuses, or (*c*) elastic waves of some nature in the head itself.

II. Purpose of the Paper.

8. The purpose of this paper is to make a preliminary survey of the evidence for the assumption that air-borne sounds communicated to one ear in the normal manner can be transmitted through the head to the other ear; and if so, to consider the further question of the details of such transmission, *e. g.*, the magnitude and the manner of the transmission.

III. Previous Work.

9. I am unable to find who first observed the fact that, if sound-waves are set up in the bony framework of the skull—*e. g.*, by pressing the butt of a vibrating tuning-fork against the teeth or the mastoid process—such vibrations can be heard; but Cappivaccius is stated to have ascribed

great diagnostic value to bone-conduction as early as 1509 *, while it is over fifty years since Mach † (1874), suggested that the phenomenon of binaural beats might be explained by assuming that the sound was conducted from one ear to the other through the bones of the head.

10. Thompson ‡ considered the possibility of such an hypothesis in 1877, three years after Mach's suggestion, of which he does not appear to have been aware ; but he dismissed it because, he argued, if the amount of bone-conduction were sufficient to account for the phenomenon of binaural beats, "There would be no reason why combinational tones should not be equally audible in binaural as in monaural audition."

11. Hermann §, 1891, also invoked the aid of bone-conduction ; while Foster ‖, in the same year, after quoting an experiment which proved that sound vibrations set up in the skull are transmitted to the stapes, proceeds as follows :—

> "Not only may vibrations be transmitted from the skull to the tympanic membrane, but also conversely the vibrations of the membrane brought about in the usual way through the meatus, may be transmitted to the bones of the skull. If a long tube introduced into one meatus be spoken or sung into, the sounds may be heard by help of a stethoscope placed over various parts of the head. They are heard best perhaps at the opposite meatus ; the vibrations of the bones of the skull set going by one tympanic membrane throw the other tympanic membrane also into vibration."

The experimental fact, that a sound introduced into one ear was heard through a stethoscope placed over various parts of the head, is of great interest. It is the first piece of experimental evidence, of which I am aware, to show that air-borne sounds can be transmitted through the head. We are not concerned with the speciousness of the argument which extracts from the fact the deduction, that the vibrations of the tympanic membrane are transmitted to the bones of the skull.

12. Then Cross and Goodwin ¶, in 1891, published the

* 'Die Krankheitendes Gehororgans,' 1827.
† Quoted by Cross & Godwin, Amer. Acad. Arts & Science, (N.S.) xix. pp. 1–12 (1891).
‡ Phil. Mag. [5] iv. p. 27 (1877).
§ Pfluger's *Archiv*, xlix. pp. 499–518 (1891).
‖ Text Book of Physiology, 1891, p. 1332.
¶ Amer. Acad. Arts & Sci., (N.S.) xix. pp. 1–12 (1891).

results of a very careful investigation they had completed, on the lines indicated by Thompson. They argued that difference tones should be heard when suitable sounds were led to the ears separately and simultaneously, if sound energy is conducted through the head to any appreciable extent. Tones were produced and conducted to the ears in various ways, viz., telephones on both ears ; a telephone at one ear and a fork at the other ; through tubes ; and by metal rods, the tones being generated by pressing the stems of forks against the rods. In none of these experiments, when the ears were stimulated separately by tones of different pitch, could difference tones be heard, whether the sounds were quiet or deafening ; but if the sound-waves were allowed to mix before reaching the ear, or if vibrations were set up in the bones of the head by putting the tuning-fork (in their second method) or one of the metal rods (in the last method) "against the head or, better, against the teeth, a loud differential tone was heard at once in the ear," which was being stimulated by aerial sound-waves.

Their conclusion was (p. 11) :

> "If there were any material bone-conduction, it certainly seems as if the very loud sounds used by us would have given evidence of it at least by the occasional production of differential tones when the sounds actuated separate ears."

13. Mader *, in 1900, carried out a long series of experiments on human heads, one of which had the top of the skull and the brain removed, while another was whole. The heads were preserved in formalin. In some of his experiments sounds were led sometimes to one ear only, and sometimes to both ears simultaneously, through rubber tubes, the ends of which were either inserted into, or fixed very close to, the meatus. A specially constructed microphone, with a needle attached to one plate, was used for detecting vibrations in selected parts of the bones of the heads. The needle was placed against the bone under examination, the fleshy covering of the bone being removed to ensure good contact. The microphone was connected to a telephone in an adjoining room, where the observer sat.

14. Mader states (p. 47) that he tested the microphone in each experiment, and that, though it was very sensitive, in none of the observations he publishes was there any trace of the sound-waves acting directly on the microphone.

* *Sitzungsber d. Kais. Akad. d. Wissens. Wien,* cix. pp. 77-35 (1900).

15. He found unmistakable evidence of vibrations in the microphone when sounds were led into or close to the ears, and concluded that air-borne waves could induce vibrations in the bones of the skull. His view was (p. 67) that the waves of compression and rarefaction in the air in the meatus and in the middle ear "produce sound-waves in the surrounding masses of bone."

16. Rostosky *, 1902, seven years later, put forward an hypothesis, to explain the phenomena of binaural beats, which was almost identical with that suggested, apparently quite independently, by Myers and Wilson in 1908 as a possible explanation of the "phase effect". Rostosky showed how, by assuming "bone conduction", the phenomena of binaural beats could be explained. But, as Stewart pointed out in 1917 †, Rostosky made a mistake of a sign, so that, according to his theory, the sound would be localized on the right when it was actually on the left, an error which Myers and Wilson avoided.

17. When Myers and Wilson ‡, 1908, proposed their hypothesis of the localization of tones by binaural differences of phase, they justified the assumption that sound entering one ear is transmitted through the bone of the head to the internal ear on the opposite side on these grounds §:

> "It is impossible to stimulate the end organs of one ear without at the same time stimulating those of the other ear. When a sound is led to one ear, not only does it pass to the cochlea of that ear but, traversing the bony vault and base of the skull, it also travels to the opposite internal ear. . . . . One is apt to neglect this bone conduction of sound from ear to ear, under conditions when two tones are led by tubes from separate rooms, one tone to each ear of the observer who sits in an intermediate room. . . . . Yet there cannot be the slightest doubt, even under these circumstances, as to the transference of each tone by bone conduction of the opposite ear."

18. In support of this statement they quote Mader's experiments and an experiment they themselves performed,

* Philos. Stud. xix. pp. 557–598 (1902).

† Phys. Rev. ix. p. 517 (1917).

‡ Proc. Roy. Soc. lxxx. A, pp. 260–266 (1908); Brit. Journ. Psych. ii. pp. 363–385 (1908).

§ Brit. Journ. Psych. ii. p. 380 (1908).

which is similar to the one described by Foster. Myers and Wilson give this account of their experiment * :—

> "It was found that an appreciable amount of sound could be sent through a person's head from one ear to the other. Ear caps with tubes attached were fitted to each ear, and a vibrating tuning-fork was held near the end of one tube. An observer listened at the end of the other tube, and with a fork of frequency 512 a distinct sound was heard, which *seemed to come* along the tube, [My italics.] The amount of sound getting through the head must, of course, be much smaller than the amount entering one ear and getting to the opposite internal ear."

In another paper † what is apparently the same experiment is thus described :—

> "We ourselves, by leading the tone of a tuning-fork to one ear of an individual, proved that an appreciable amount of sound could be transmitted through his head to the other ear and could thence be conducted by a tube so as to be audible to the ears of a second observer."

19. In 1912, Nikiforowsky ‡ endeavoured to obtain experimental evidence of the transmission of sound through the head. He employed a specially constructed microphone, isolated in lead, to detect sound vibrations under three different conditions.

(*a*) When the sound was produced by the subject speaking or singing;
(*b*) When the sounding body, *e.g.* a tuning-fork, was outside the subject's body, but was in direct contact with the head;
(*c*) When aerial sound-waves impinged on the head.

His results showed that, with (*a*), the flow of energy is greatest through the nose and mouth and that "the quantity of energy flowing from the ears is relatively large" (p. 196), while comparatively little energy flows from the hard parts of the head;

> With (*b*), "the hard parts of the head propagate the sound better than the soft, and the sound energy flowing from the ears exceeds, under the same conditions, that from the other parts of the head" (p. 197).

* Proc. Roy. Soc. lxxx. A, p. 266 (1908).
† Brit. Journ. Psych. ii. p. 381 (1908).
‡ *Zeit. f. Sinnes Physiol.* xlvi. pp. 179-192 (1912).

With (*c*), in spite of "very numerous and diverse experiments" with sounds "as strong as possible" he could obtain nothing positive, and concluded that the amount of sound which could penetrate inside the head was exceedingly small.

20. Peterson *, carried out an inquiry into "The Nature and Probable Origin of Binaural Beats" in 1916, and also included in his investigation an extensive series of experiments on an observer who was deaf in one ear. By no method could he obtain any evidence that aerial sound-waves, impinging on one ear, could excite the other ear also. He states his conclusions thus (p. 349):—

> "Binaural beats and the perception of phase differences [cannot] be explained on the basis of conduction of the sound wave from ear to ear through the skull. . . . . Both of these phenomena seem to be cortical in origin, while monaural beats probably originate in the basilar membrane. Combination tones, both subjective and objective, are in all probability objective in origin to the basilar membrane."

21. Stewart (1917, 1920, and 1922), while maintaining that bone-conduction cannot be a possible explanation of the general phenomena of binaural beats or lie at the basis of our perception of phase †, nevertheless falls back on such transmission as an explanation of the maxima and minima of intensities he perceived in binaural beats ‡.

IV. Remarks on this Work.

22. The only direct evidence I have been able to discover, which is adduced as proof of the transmission of aerial-bone sound-waves through the head, is contained in the experiments described by (*a*) Foster (para. 11); (*b*) Mader (paras. 13–15); and (*c*) Myers and Wilson (paras. 17, 18).

23. Mader's evidence is very direct and emphatic. The account he gives of his experiments leaves little room to doubt his observations. He was, admittedly, working with dead heads; but, if sound-waves can be set up in the bones of a dead head by aerial vibrations led into the ears, there is every possibility that they can similarly be produced in the bones of the living head. Against this evidence, however, we must set that of Nikiforowsky, whose results

* Psych. Rev. xxiii. pp. 333–351 (1916).

† Phys. Rev. xv. pp. 425–445 (1920).

‡ Psych. Monog. xxv. pp. 31–46 (1917–18); Phys. Rev. ix. pp. 502–528 (1917).

were negative. Nikiforowsky worked with the living head, and with a microphone which was carefully shielded from air-borne sound-waves, which Mader's was not. The experiment should be repeated, preferably by a psychologist. With the powerful means of attack which are now available, it should be possible to obtain data which will either prove or refute Mader's results. I hope to carry out such an investigation in the near future.

24. As regards Myers and Wilson's experiment, the lack of details of the measures taken to prevent the sound from reaching their observer by ordinary air paths makes one hesitate to accept the observations as proof that "an appreciable amount of sound could be transmitted through" an individual's head. Their observations, and the similar ones by Foster, require confirmation; especially in view of the evidence produced by Peterson that he could not make his monaural subject hear a note led to his deaf ear when the normal ear was plugged. If the deductions drawn by Foster and by Myers and Wilson from their observations are correct, that is if the sounds heard by them had actually travelled through the head of their subject, it is difficult to understand why Peterson's monaural subject could not hear a sound introduced into his deaf ear.

V. My Experiments.

25. I have accordingly repeated the observations of Foster and of Myers and Wilson, with the modifications I indicate later. I have also repeated the experiment of Cross and Godwin, to see if I could find any evidence for the transmission of sounds through the head by the detection of difference tones when the primary tones were led separately and simultaneously to the ears.

(A) *Direct observation of Sound transmitted through the Head.*

(a) *Experiment and Results.*

26. I at first attempted to repeat Foster's experiment, the subject and observer being together in the sound-proof room.

The sound was produced by a telephone at the subject's ear. I endeavoured to isolate the sound, so that it could not be heard by another person in the sound-proof room. In this I was quite unsuccessful with the means at my disposal, unless I made the sound very quiet. This would obviously make it very difficult to detect the sound, after

transmission through the head. I therefore turned my attention to the observer. He was provided with an ordinary stethoscope, as in the experiment described by Foster, with which he explored the subject's head. Preliminary experiments showed that the observer was by no means isolated from sound. Even when he pressed the mouth of the stethoscope firmly against the fleshy part of his thumb, he could still hear the subject speak, and he could still hear a vibrating tuning-fork or telephone held in the subject's hand, though the loudness was considerably decreased. If the subject held the vibrating tuning-fork or telephone near one ear, the observer could clearly hear the note when he held the stethoscope near to, or touching, the subject's head. If the observer now placed the stethoscope receiver against the subject's head the loudness of the sound decreased, and at times could not be heard at all, if the rim of the receiver made good contact all round its circumference with the head. This decrease in loudness was observed whatever the part of the head to which the stethoscope receiver was applied, provided the contact between the receiver and the head was sufficiently good.

27. The experiment was now repeated under conditions which, without any doubt, gave rise to bone-conduction. Bone-conduction was obtained by the subject holding a gently vibrating tuning-fork between his teeth. With the receiver of the stethoscope near the head, the observer either could not hear the fork at all or else he heard it but faintly ; with the stethoscope receiver in contact with the head the sound became much louder, while, if the receiver were pressed on a bone, the fork was heard very distinctly and could be heard sometimes even after the subject had ceased to hear it. This depended, apparently, on the relative auditory acuity of the subject and of the observer.

28. It might be argued that these experimental results can be explained as follows. The pressure of the mouth of the stethoscope in the first experiment prevents the bone from vibrating, and so the sound grows quieter as the pressure increases : in the second experiment the osseous vibrations are so great that they are not damped by the pressure. This explanation is not, I think, very probable In the first experiment the loudness of the sound heard by the observer decreased very perceptibly whenever there was good contact between the stethoscope receiver and the head. Pressure was only necessary when good contact was otherwise impossible owing to the unevenness of the surface. In the second experiment the sound of the tuning-fork held

between the teeth could be heard, when the stethoscope was pressed against the mastoid process. Sometimes the sound could be heard by the observer for a longer time than the subject himself could hear it, that is when the amplitude of the osseous vibrations was too small for the subject to appreciate the sound.

(b) *Conclusion.*

29. These experiments would seem therefore to support Nikiforowsky's finding, and to throw doubt on the validity of Foster's and of Myers and Wilson's deductions, (*a*) that aerial sound-waves of ordinary intensity can be transmitted through the head so as to be heard on the other side, and (*b*) that the transmission is due to bone-conduction. No matter how the sounds reached their observers it would seem clear that they were not transmitted by bone-conduction.

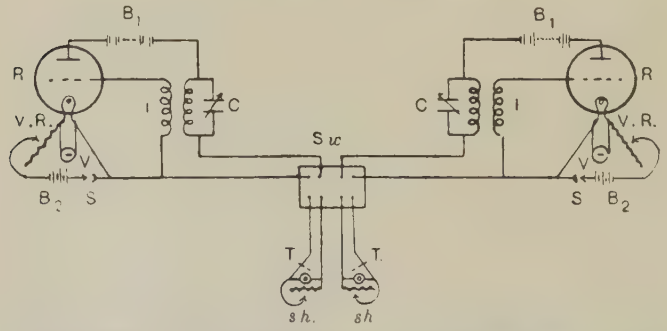
(B) *Difference Tone Experiment.*

30. My Difference Tone Experiment is a repetition of that performed by Cross and Godwin. The only variation is in the apparatus used.

(a) *Apparatus.*

31. The tones were produced by telephones in oscillating circuits *, as shown diagrammatically in fig. 1.

Fig. 1.—Diagram of Apparatus.



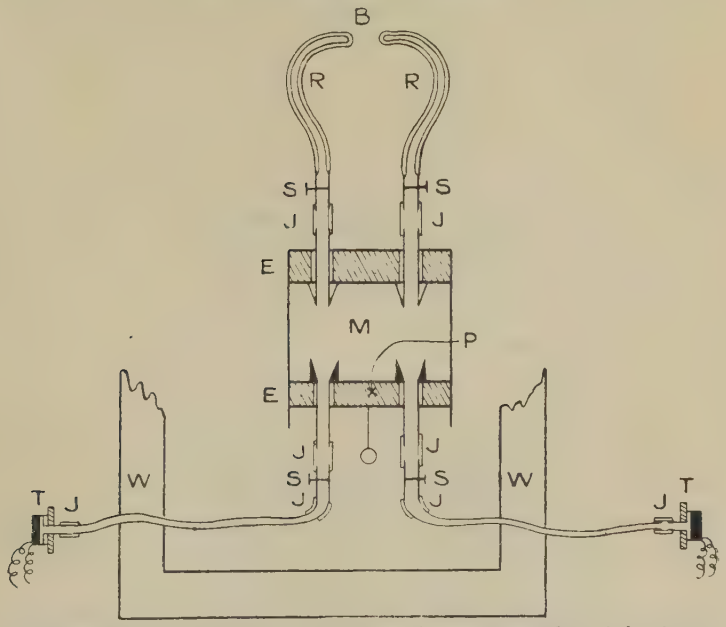
B_1. High Potential Battery (54 volts). B_2. Accumulator (6 volts) C. Variable Condenser. I. Inductances. R. Valve. S. Switch *sh.* Shunt. T. Telephone. V. Voltmeter. V.R. Variable Resistance *Sw.* 4-way Switch, by means of which the telephones can be connected to either circuit.

* A full description of the apparatus will be found in the British Journ. Psychology, xv. pp. 280–307 (1925). I am indebted to Prof. E. V. Appleton for the suggestion to use this apparatus in experiments on sound.

32. The two circuits were screened from one another by placing the one circuit into a galvanized iron cylinder. The cylinder, which is about 85 cm. long and 48 cm. in diameter (external measurements), has a double wall of galvanized iron about 2 mm. in thickness, with one thickness of iron at its base. It has no top *.

33. The sounds from the telephones were led, through metal composition tubing, into the sound-proof room, fig. 2.

Fig. 2.—Diagram of Apparatus.



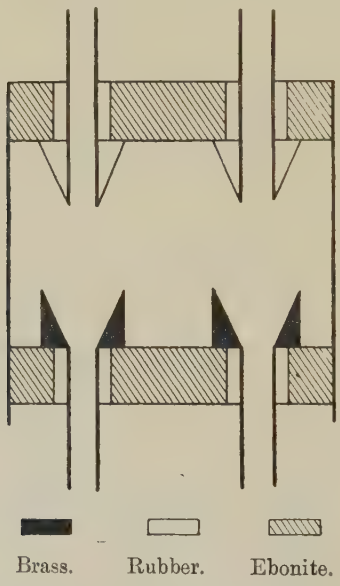
B. Binaurals. E. Ebonite. J. Rubber joints strengthened by insulation tape. M. Mixing Chamber. S. Stop-cock. P. Movable Piston. T. Telephone. R. Rubber tubing. W. Walls of Sound-proof Room.

* (1) From the observations of Smith-Rose, Proc. Phys. Soc. xxxiv. pp. 127-138 (1922), I anticipated that there would be difficulty in screening the circuits. I found no trace of interaction between the circuits which were in separate rooms on either side of the sound-proof room, at a distance of about 4·5 metres apart. The inductances were in approximately the same plane, and the axis of the cylinder, in which one oscillating set was enclosed, was at right angles to this plane. I made no investigation of the amount of screening effected.

(2) I found that the circuit in the iron cylinder gave a note of the frequency of the oscillations, even if no telephone was in the circuit. This effect may be similar to that pointed out by Köhler, that if an oscillating current of sufficient strength is transmitted through an ordinary telephone circuit a note of the frequency of the oscillating current may be heard even if the telephone diaphragm is removed.

The tubing was joined to short brass tubes, which fitted tightly into the holes in the ebonite telephone ear-pieces, by stout rubber tubing, strengthened by a wrapping of insulation tape. The metal parts were put into as close contact as was possible. All joints were made in this manner. Stop-cocks were fixed at the ends of the tubing, so that the sounds could be cut off before reaching the mixing chamber; the sounds could also be cut off from both or either of the tubes leading to the specially constructed stethoscope binaurals, by closing the stop-cocks on the further side. The mixing chamber, fig. 3, consisted of a brass cylinder

Fig. 3.—The Mixing Chamber.



about 11 cm. long and 11 cm. in diameter. The one end was permanently closed with an ebonite plate through which two brass tubes, embedded in rubber, projected; the other end was fitted with an ebonite piston, which also carried two tubes, embedded in rubber. The whole was very accurately made and the piston had a guiding groove, to ensure that the brass tubes it carried fitted exactly over the tubes in the base. The ends of these brass tubes were bevelled and the inner ones were covered with rubber so that the joints, when the pistons were pushed home, were air-tight.

(b) *Method of Experiment.*

34. When experimenting, the observer sat in the sound-proof room with his back to the table on to which the "mixing chamber" was screwed. The experimenter stood at the other side of the table and, by moving the piston, and opening or closing one or other of the taps he could present (1) either sound to one or to both ears; or (2) the two sounds separately, one to each ear; or (3) the two sounds, mixed together, to both ears, or to one ear only (*vide* fig. 4).

Fig. 4.

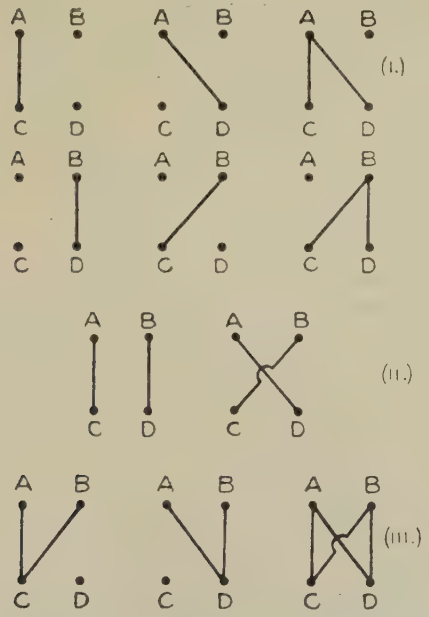


Diagram showing the possible ways in which the sounds (A, B) could be presented to the observer's ears (C, D).

The tones used had frequencies of 879 and 763 d.v./sec. so the first difference tone was a low note of 116 d.v./sec. Observers were first given the two notes separately, and were then told that they would be given the two notes together, and that they must listen particularly for the difference tone, the pitch of which was sung. When this had been recognized the experiment began. The tones were either presented separately to each ear, or were mixed in the mixer before reaching the ears, and the observer

simply reported whether the difference tone was discerned or not.

(c) *Experimental Results.*

35. Five subjects were experimented on, and various other observers were tried to see if anyone could be found who could hear the difference tone when the tones were led separately to the ears. No such individual was discovered, even though the sounds were made so loud as to be uncomfortable. But if one of the binaurals was removed, and, instead, a feebly vibrating tuning-fork was held with its stem between the teeth or pressed against the bony framework of the head while an appropriate tone was led to the ear through the remaining binaural, a difference tone was clearly discriminated at the ear in which the binaural was.

36. Later I substituted a brass stop-cock, fig. 5, for the

Fig. 5.

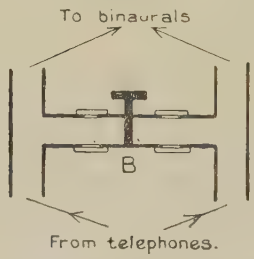


Diagram showing the brass Stop-cock (B) which was substituted for the Mixing Chamber, *vide* fig. 2.

mixing chamber, so that, when the cock was closed, the two trains of waves were separated by the brass of the stop-cock and two very thin layers of vaseline, used for lubrication purposes, on each side of the brass. If aerial sound-waves are to be assumed capable of exciting vibrations in the bony framework of the skull and of thus being communicated to the other ear—which appears to be the view of Mader—"*a fortiori*" must they be conducted through the brass *.

* Recent experiments by Hahnemann, Hecht, and Lichte (*Zeit. Techn. Physik*, iv. pp. 93–99, 1923, have demonstrated the enormous difficulty with which sound-waves in the air can set up vibrations in a contiguous solid, and vice versa. Even with such an ideal substance as water, these experimenters found that only one-thousandth of the energy could, under the most favourable conditions, be transmitted from water to air or from air to water.

But no difference tone could be heard if the stop-cock in the connecting tube were closed. If, however, the cock were opened, ever so little, the difference tone immediately sprang into evidence. No quantitative measurements of the intensities were made, but, subjectively judged, a weak sound mixed with a much louder sound gave an easily discernible difference tone.

(d) *Conclusions.*

37. These experiments bear out fully the observations of Thompson, Cross and Godwin, and Peterson. Difference tones could not be heard when notes of suitable frequencies were led to the ears separately and simultaneously.

38. The conclusions to be drawn will depend on the theory of hearing to which one subscribes.

39. Difference tones will be produced when an asymmetrical system is subjected to two impressed harmonic forces. Such an asymmetrical system exists in the tympanum, which, according to one school, creates the difference tones normally heard when two notes of suitable frequencies and intensities are sounded. Adherents of this school would probably agree (*a*) that the experiment shows that the far tympanum was not set into vibration by sounds which had been transmitted through the head; (*b*) but that it by no means rules out the possibility of sounds being transmitted through the head from one ear to the cochlea on the other side. Another school, which might postulate the cochlea as a possible seat for the production of difference tones, would consider the evidence of this experiment as being more antagonistic still to any hypothesis of the transmission of sound through the head.

40. Adopting the point of view of the former school, it might be argued that Myers and Wilson, *cf.* paras. 17, 18, stated the necessity for bone-conduction over strongly; that it would be more correct to say that some sound is conducted through the head, but that the amount is relatively small, and that in consequence the difference tone produced at the tympanum is so weak that it cannot be appreciated.

(C) *Remarks.*

41. Wegel and Lane *, in an account of experiments published in 1924, give data which are of interest to us

* Phys. Rev. xxiii. pp. 266–285 (1924).

from the point of view of the transmission of sound through the head. They found that, if two tones were introduced into the same ear, and if the "pressure" * of the one tone was increased, a certain "pressure" would prevent the second tone from being heard. If now the tones were led separately, one to each ear, the "pressure" of the first tone had to be increased in the ratio of $1 : 10^2$ to $1 : 10^3$ before masking occurred. From this they infer, without sufficient justification in my opinion, that the masking is peripheral, that it is "caused by the conduction of the masking tone through the head" by bone-conduction. They also report "that people very deaf in one ear have been noted for which 10^2 or 10^3 times the current is required for audition with the receiver on the deaf ear over that for the receiver on the good ear"; and that "when the sound for the receiver on the deaf ear is audible, it may be greatly enhanced by placing the finger in the good ear, indicating that the sound is not only heard first in the good ear, but that it arrives there by bone-conduction." It may be that, as Wegel and Lane suggest, there is transmission of sound of this order of magnitude through the head from one ear to the other and that the masking is in some way due to this transmission; but that the masking *is* due to the transmission is pure assumption, and Minton † very properly objects to such assumptions being made in the present state of our knowledge. The further inference, that there is *bone-conduction*, is altogether unwarranted. Assuming the transmission there is nothing, in these experiments, to show that it is due to bone-conduction rather than to other possible means of transmission.

42. In this connexion an interesting little experiment was described by Thompson in 1878 ‡. Thompson states that if a small vibrating tuning-fork

> "be pressed against the parietal or occipital regions of the head on the right of the median line, its sound appears to be heard in the left ear. . . . If, however, the fork be pressed against the region immediately above either temporal bone, its sound is heard in the ear of the same side."

* Wegel and Lane define the magnitude of a tone as "the ratio of its pressure of that of its minimum audible value."

† Phys. Rev. xxii. pp. 506–509 (1923).

‡ Phil. Mag. [5] vi. p. 390 (1878).

43. I have tried this experiment with forks of frequencies 50, 256, 435, 800, and 1000 d.v./sec. I find it very difficult to judge the position of the sound heard when the fork is pressed against the region immediately above either temporal bone; but if any of the above forks, sounding so faintly as to be inaudible when held over the head in the sound-proof room, is pressed on the lateral bones immediately above the right ear, (the fork being so held that the vibrations of the prongs are at right angles to the line joining the ears and the whole of the fork being on the right of the sagittal plane so that the right ear has any advantage which may accrue from the aerial sound-waves leading in phase), the sound is immediately heard and is located on the *left*, i. e., on the further side. If the fork is pressed against the mastoid process behind the right ear, the tone is located on the right. Thompson simply notes the experimental fact, without giving any explanation; and I am equally at a loss for an explanation in conformity with the generally accepted physiological assumption that a sensation can be aroused by the appropriate stimulus only if it acts on the end organ.

V. Summary.

44. This preliminary survey shows that little or no reliable experimental evidence has so far been obtained to support the hypothesis that aerial borne sound-waves of normal intensity, which reach one ear through the auditory meatus, are transmitted through the head to the other ear. I hope to attack the problem in the near future and, with the assistance of the recently perfected means of amplifying electrical currents, it may perhaps be possible to obtain positive results.

45. Till transmission has been proved, it is rather previous to consider how the vibrations are initiated and whether transmission takes place through the bones, the sinuses, the soft parts of the head, or through any combination of these.

XII. *Minimization of Magnetic Leakage and of its Effect in the Magnetic Testing of Bars and Rods.* By Edward Hughes, *B.Sc., Ph.D., A.M.I.E.E.**

Abstract.

A modified form of the Iliovici permeameter is described in which the balance of magnetic potential is determined by a movable yoke. Experimental results are given showing that the magnetic leakage in the specimen under test varies considerably with the flux density and is dependent upon the disposition of the magnetizing coils. Tests performed on mild-steel and cobalt-chrome specimens indicate that the leakage is greatly affected by the permeability of the sample. The influence of the width of the search-coil upon the accuracy of magnetic testing is discussed mathematically. It is shown that a very large error in the determination of the magnetizing force for a given flux density may be involved if the search-coil is narrow; whereas, with a search-coil extending over the length of bar under test, the error is reduced to a small value. Curves are given showing the percentage errors involved with the extended search-coil for different leakages and different flux densities, the flux density being expressed as a fraction of the saturation density.

In the double bar and yoke method of magnetic testing it is impossible to eliminate magnetic leakage, though it may be reduced by the addition of compensating coils as in the Burrows permeameter. The latter, however, presupposes the four joints to be of equal reluctance—a condition that is often difficult to fulfil. Burrows † has pointed out that, with two soft-iron bars tested by the double-bar method, the magnetic leakage between the centres of the bar and of the yoke may amount to 5 per cent.; and it is surprising that so little attention appears to have been devoted to the influence of magnetic leakage upon the accuracy of magnetic testing and to the dependence of the error upon the length of the search-coil.

The tests to be described were performed on bars of mild steel and of cobalt-chrome steel by means of a modified form (fig. 1) of the permeameter described in the 'Proceedings' of the Physical Society of London'‡. The apparatus is shown diagrammatically in fig. 2, where *TT* represents the bar to be tested and *A* is a magnetizing coil situated between the two prongs of a movable yoke *Y*. Another magnetizing

* Communicated by the Author.

† "Determination of Magnetic Induction in Straight Bars," Bull. Bureau of Standards, vi. p. 31.

‡ "A Magnetic Bridge for testing Straight Specimens," Physical Soc. Proc. xxxvii. p. 233.

Fig. 1.

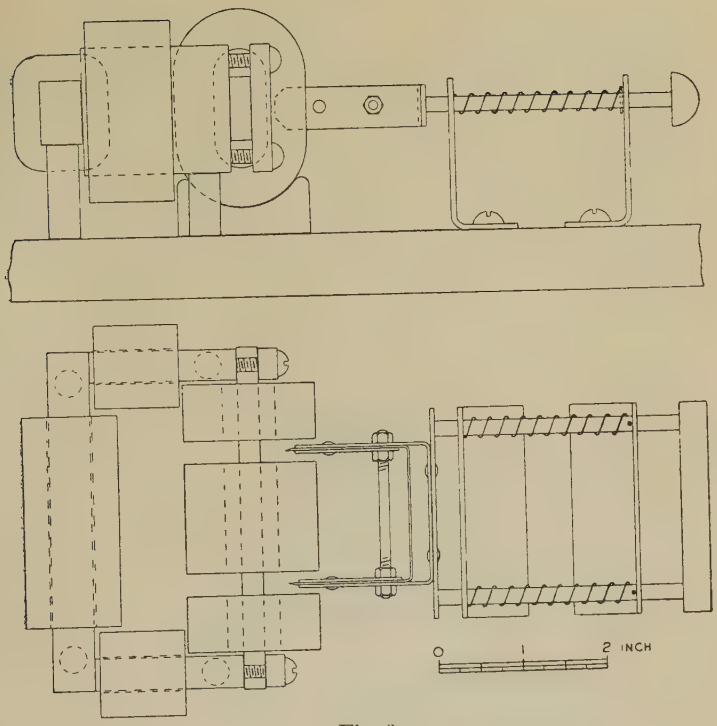
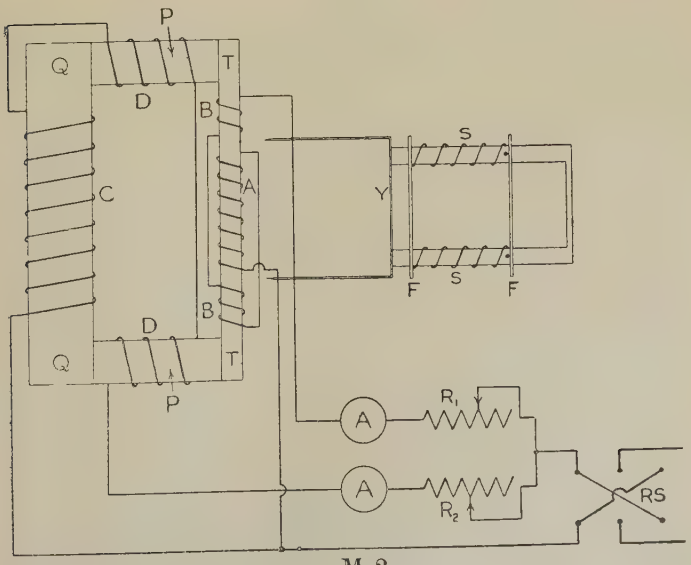


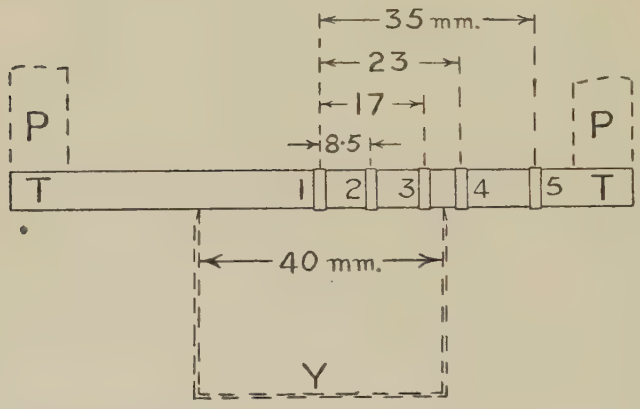
Fig. 2.



M 2

coil *BB* is wound in two sections, one on each side of *A* with sufficient clearance to allow of *Y* being moved backwards and forwards. The magnetic circuit of *TT* is completed through iron yokes *PP* and an iron core *QQ* having windings *DD* and *C* respectively. The coils are connected so that their m.m.f.'s are all acting in the same direction. Five search-coils, each of ten turns, 36 S.W.G., were wound on *TT* in positions indicated in fig. 3. The movable yoke *Y*

Fig. 3.



consists of a strip of Stalloy, 0·5 mm. thick, held by brass plates (fig. 1) which are carried by two rods passing through guide plates *FF* with light springs *SS* to draw *Y* away from *TT*.

The operation of the apparatus is as follows:—With a given current through coils *A* and *B*, the current through *C* and *D* is adjusted until no deflexion is obtained on a galvanometer connected to search-coil 1 when the auxiliary yoke *Y* is moved up to *TT*. When a balance has been thus obtained, the points of contact of *Y* with *TT* are at the same magnetic potential, and the m.m.f. of coil *A* is absorbed in sending the flux through that portion of *TT* that lies between these points of contact.

The leakage flux is then measured by reversing the magnetizing currents and noting the deflexions with coils 2, 3, 4, and 5 respectively connected in opposition to coil 1. This leakage flux has been expressed as a percentage of the flux through coil 1; and the results for the mild-steel bar are given in fig. 4. The above test was repeated with different magnetizing currents. It will be observed that both the magnitude and the distribution of the leakage flux

vary with different currents and are dependent upon the permeabilities of the specimen and of the yoke.

Fig. 4.

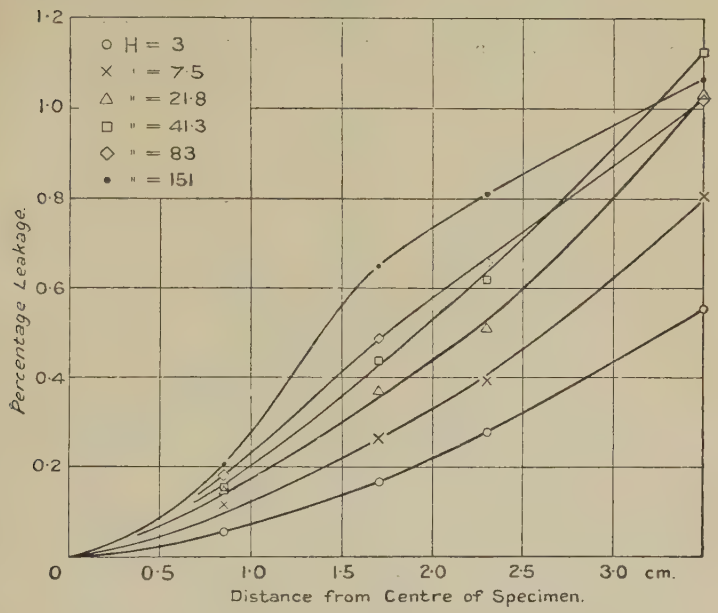


Fig. 5.

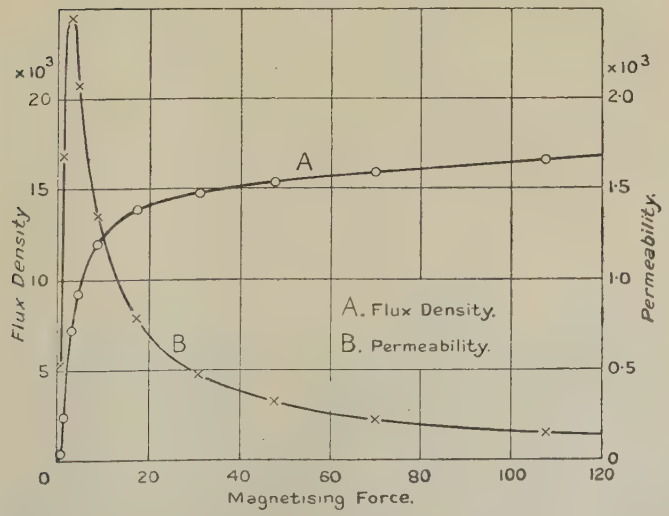
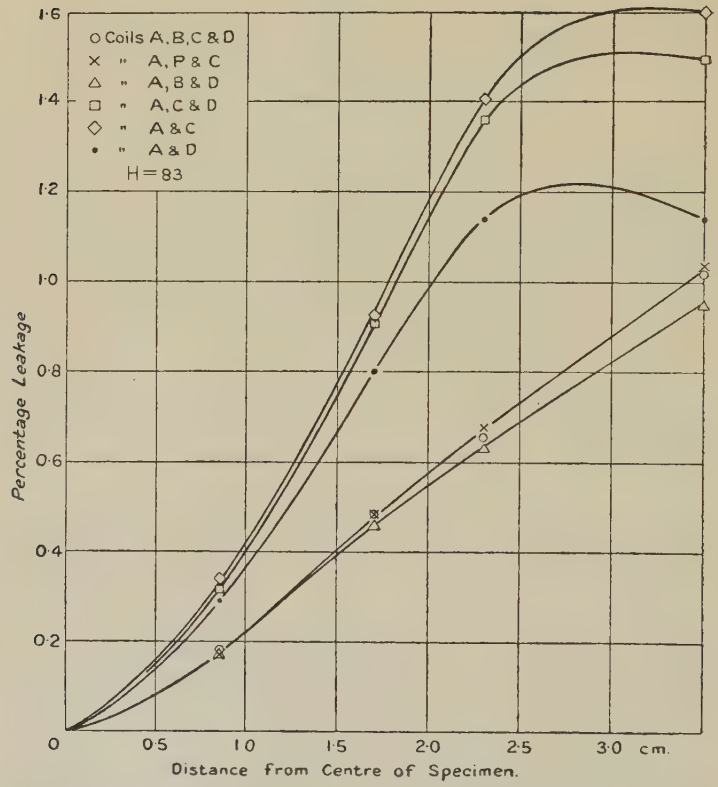


Fig. 5 has been included to show how the flux density and the permeability of this mild steel bar varied with the magnetizing force.

The influence of coils B, C, and D upon the leakage was next investigated. The current through A (and through B when the latter was in circuit) was kept constant at a value corresponding to H = 83, and that through C or D, or both, was varied until search-coil 1 indicated a balance as already described. The curves in fig. 6 show the percentage leakages

Fig. 6.



with different combinations of coils, and indicate clearly that the leakage is practically the same whether both C and D or only one of them be in circuit—in other words, that only one of these coils need be employed. The curves also indicate the important contribution of coil B towards the reduction of the magnetic leakage—particularly in that portion of the bar that lies inside coil A.

Similar tests were carried out on a bar of cobalt-chrome steel, the latter being chosen owing to its low permeability.

The results are plotted in figs. 7 and 8, and fig. 9 shows the variation of B and μ with H for this particular specimen. These figures confirm the conclusions derived from the tests on mild steel, and at the same time emphasize the influence

Fig. 7.

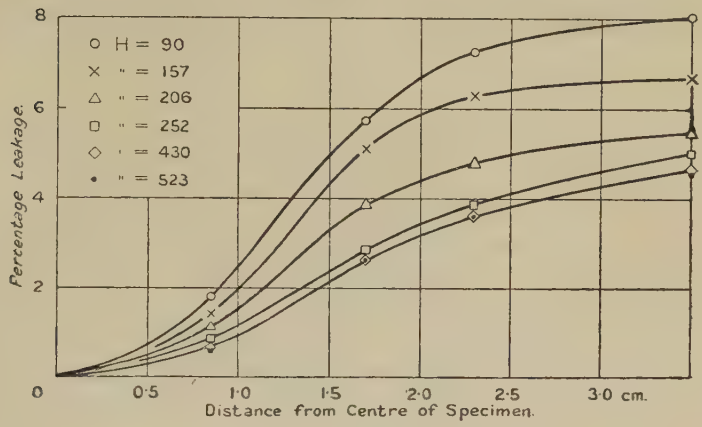
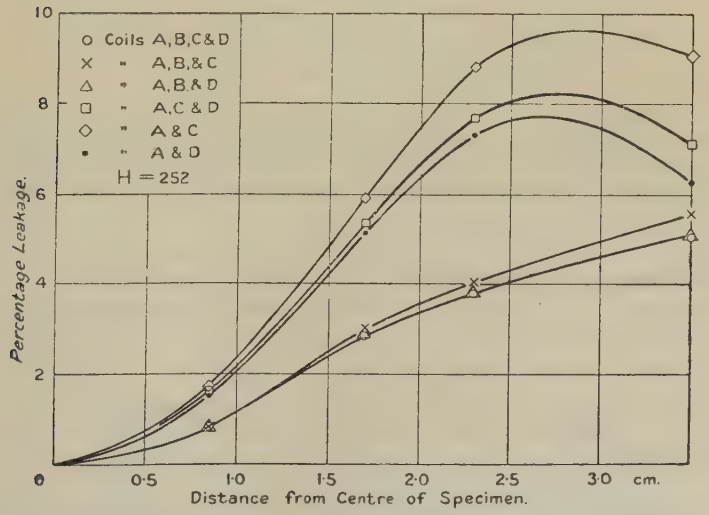


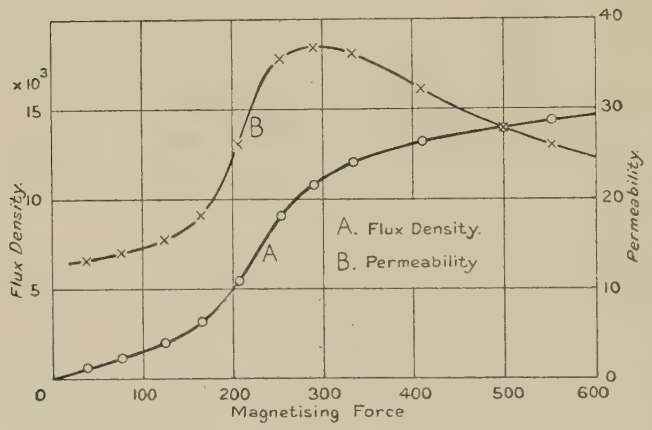
Fig. 8.



of permeability on the magnetic leakage. It will now be obvious that in order to minimize the magnetic leakage in this type of magnetic tester, it is necessary to wind the magnetizing coil over as great a length as possible of the specimen. Windings placed on the yokes, however, contribute practically nothing towards the reduction of leakage.

It is now essential to consider the extent to which the width of the search-coil affects the error introduced by the existence of magnetic leakage. If the coil be narrow and wound midway along the specimen, it will obviously be measuring the maximum flux density, whereas the magnetizing force calculated from the ampere-turns on the coil is less than that corresponding to the maximum flux density.

Fig. 9.



On the other hand, if the search-coil is wound over the length of bar under test, the mean flux density is obtained. Neither of these alternatives is quite correct; and we shall now proceed to compare their results with that obtained by integrating the magnetizing force over the length under test.

From figs. 4 and 7 it is evident that over the distance spanned by the prongs of Y (fig. 3) the leakage curves are intermediate between linear and parabolic curves. We shall therefore consider two cases:—

(*a*) When the leakage flux varies directly as the distance from the centre of the specimen.

(*b*) When the leakage flux varies as the square of the distance from the centre of the specimen.

Case (*a*).

Let $2l$ be the length of bar under test, *i. e.* the distance between the prongs of yoke Y (fig. 2). Let B_m be the maximum flux density and B_x the flux density at distance x

from the centre (fig. 10). Let s be the magnetic leakage—expressed as a fraction of B_m—at distance l from centre. Then

$$B_x = B_m(1-sx/l).$$

If T be the number of turns on a search-coil occupying length $2l$,

$$\text{flux linkages over length } dx = B_m(1-sx/l)\frac{T\,dx}{2l},$$

$$\therefore \quad \text{total flux linkages} = 2\int_0^l \frac{B_m T}{2l}\left(1-\frac{sx}{l}\right)dx$$

$$= B_m T(1-s/2).$$

If B_{av} be the average flux density,

$$B_{av} = B_m(1-s/2).$$

If H_{av} be the magnetizing force corresponding to B_{av},

$$\text{Reluctivity} = \frac{H_{av}}{B_{av}} \fallingdotseq a + \frac{H_{av}}{B_s} = a + bH_{av}\,*,$$

where B_s = saturation density = (say) $1/b$,

and a = a constant for a given specimen.

Also, $bB_m = B_m/B_s$; so that the term bB_m, which occurs frequently in the following calculations, represents *the ratio of the flux density at the centre of the bar to the saturation density of the material.*

Substituting for B_{av} in the above expression, we have

$$H_{av} = \frac{aB_m(1-s/2)}{1-bB_m(1-s/2)},$$

$$\text{and total m.m.f.} = 2H_{av}l$$

$$= \frac{2laB_m(1-s/2)}{1-bB_m(1-s/2)}. \quad . \quad . \quad . \quad . \quad (1)$$

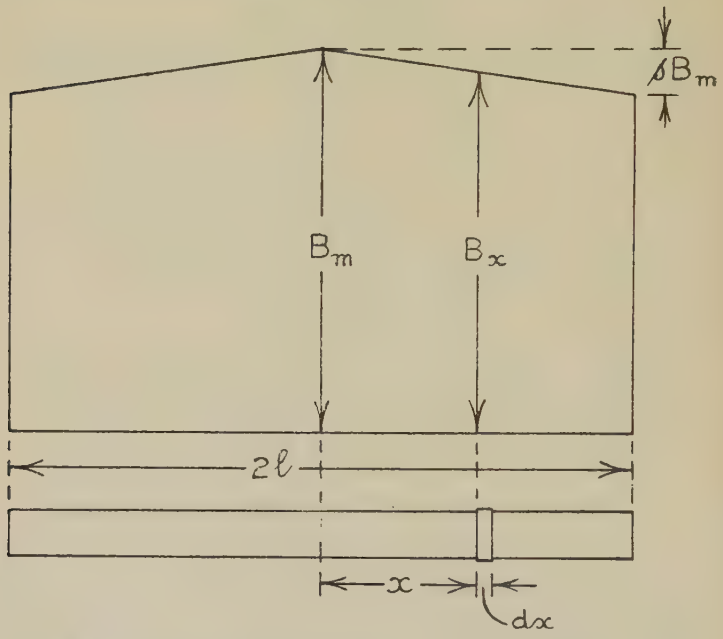
Hence we can calculate in terms of B_m the m.m.f. that would be required if the flux density were uniform along the specimen at the mean values given by a search-coil of length $2l$. Thus, if s be 0·05 and B_m be 0·8 of the saturation density,

$$\text{total m.m.f.} = 8{\cdot}865laB_m. \quad . \quad . \quad . \quad . \quad (2)$$

* For simplicity, the actual flux density is used instead of the ferromagnetic den ity.

Let us now calculate the actual m.m.f. required when the flux is distributed as shown in fig. 10.

Fig. 10.



If H_x be the magnetizing force corresponding to flux density B_x in the above figure, then

$$\frac{H_x}{B_x} = a + bH_x.$$

Substituting for B_x in terms of B_m, we have

$$H_x = \frac{aB_m}{1-bB_m} \times \frac{1-\frac{sx}{l}}{1+\frac{bB_m sx}{l(1-bB_m)}},$$

$$\therefore \text{ total m.m.f.} = 2\int_0^l H_x dx$$

$$= \frac{2al}{b^2 sB_m} \log\left(1+\frac{bB_m s}{1-bB_m}\right) - \frac{2al}{b}$$

$$= \frac{alB_m}{1-bB_m}\left\{2 - \frac{s}{1-bB_m} + \frac{2}{3}\cdot\frac{s^2 bB_m}{(1-bB_m)^2} - \frac{2}{4}\cdot\frac{s^3 b^2 B_m^2}{(1-bB_m)^3} + \ldots\right\}. \quad (3)$$

Taking the values of $s=0{\cdot}05$ and $b\mathrm{B}_m=0{\cdot}8$ assumed on p. 169, and substituting in the above expression, the terms being continued until negligibly small, we have

$$\text{total m.m.f.} = 8{\cdot}895al\mathrm{B}_m. \quad . \quad . \quad . \quad . \quad (4)$$

Comparison of (2) and (4) shows that for these particular values of the leakage and of the flux density, the m.m.f. corresponding to the mean flux density is 0·34 per cent. less than the m.m.f. calculated for a linear variation of the flux density.

Values of the m.m.f. have been calculated from expressions (1) and (3) for different values of leakage and of flux density ; and the difference between the corresponding values has been expressed as a percentage of the m.m.f. calculated from (3). For instance, with

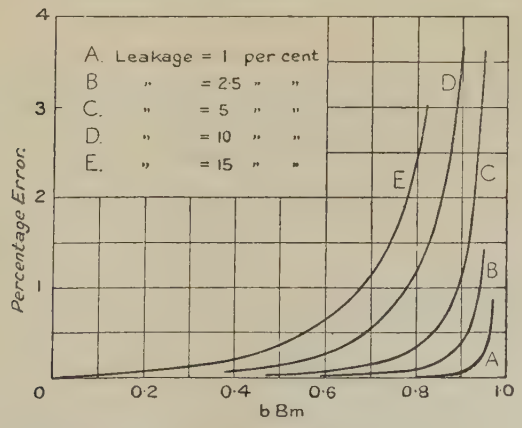
$$s = 0{\cdot}05 \text{ and } b\mathrm{B}_m = 0{\cdot}8,$$

$$(\text{m.m.f.})_1 = 8{\cdot}865al\mathrm{B}_m,$$

and $$(\text{m.m.f.})_3 = 8{\cdot}895al\mathrm{B}_m.$$

The difference between the two expressed as a percentage of $(\text{m.m.f.})_3$ is 0·34. These results have been plotted in fig. 11,

Fig. 11.



from which it follows that with flux densities less than 90 per cent. of the saturation value, the error involved in the determination of the m.m.f.—even for a leakage of 5 per cent.—can be limited to 1 per cent. by merely winding the search-coil over the length of specimen under test.

It may be added that in magnetic testing the flux density

is seldom taken up to 90 per cent. of the saturation value. Also, at high flux densities, the expression given above for the magnetic reluctivity is only approximate, since it neglects H in comparison with B; whilst heterogeneity of the material causes the slope * of the reluctivity curve to decrease.

Had the search-coil been narrow and wound halfway along the specimen, the maximum flux density B_m would have been measured. If H_m be the true magnetizing force for this flux density, then

$$\frac{H_m}{B_m} = a + bH_m,$$

$$\therefore \quad H_m = \frac{aB_m}{1-bB_m},$$

and total m.m.f. for a length $2l = \dfrac{2laB_m}{1-bB_m}$

$$= 10laB_m \text{ for } bB_m = 0{\cdot}8,$$

a value that is 12·4 per cent. greater than the m.m.f. as calculated from the distribution of flux by expression (3). This is sufficient to show the enormous error that may be introduced by the use of a narrow search-coil.

Case (*b*).

The leakage flux is assumed to vary as the square of the distance from the centre of the specimen. Using the same symbols as before, we have from fig. 12,

$$B_x = B_m - \left(\frac{x}{l}\right)^2 sB_m,$$

$$\therefore \text{ total flux linkages} = 2\int_0^l \frac{B_m T}{2l}\{1-(x/l)^2 s\}dx$$

$$= B_m T(1-s/3).$$

If B_{av} be the average flux density,

$$B_{av} = B_m(1-s/3).$$

* Physical Soc. Proc. xxxvii. p. 238.

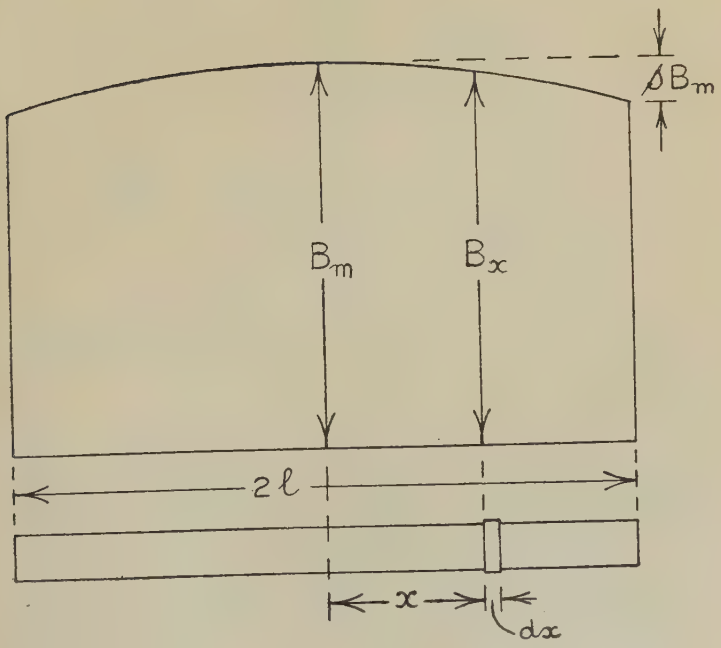
But $$\frac{H_{av}}{B_{av}} = a + bH_{av},$$

$$\therefore \quad H_{av} = \frac{aB_m(1-s/3)}{1-bB_m(1-s/3)},$$

and total m.m.f. $= 2lH_{av}$

$$= \frac{2laB_m(1-s/3)}{1-bB_m(1-s/3)}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fig. 12.



For example, if s be 0·05 and bB_m be 0·8, as on p. 169,

$$\text{total m.m.f.} = 9{\cdot}2166laB_m. \quad . \quad . \quad . \quad . \quad (6)$$

Let us now calculate the actual m.m.f. for the assumed flux distribution (fig. 12),

$$\frac{H_x}{B_x} = a + bH_x.$$

Substituting for B_x, we have

$$H_x = \frac{aB_m\left(1-\frac{sx^2}{l^2}\right)}{(1-bB_m)\left\{1+\frac{bB_m\,sx^2}{l^2(1-bB_m)}\right\}},$$

$$\therefore \text{ total m.m.f.} = 2\int_0^l H_x\,dx$$

$$= \frac{2aB_m}{1-bB_m}\left\{-\frac{l(1-bB_m)}{bB_m}\right.$$

$$\left.+\frac{l}{bB_m}\sqrt{\frac{1-bB_m}{bB_m s}}\cdot\tan^{-1}\sqrt{\frac{bB_m s}{1-bB_m}}\right\}$$

$$= \frac{2alB_m}{1-bB_m+bB_m s}\left[(1-s)\right.$$

$$+\frac{s}{1-bB_m+bB_m s}\left\{\frac{2}{3}+\frac{2.4}{3.5}\left(\frac{bB_m s}{1-bB_m+bB_m s}\right)\right.$$

$$\left.\left.+\frac{2.4.6}{3.5.7}\left(\frac{bB_m s}{1-bB_m+bB_m s}\right)^2+\ldots.\right\}\right]. \quad (7)$$

Taking $s=0{\cdot}05$ and $bB_m=0{\cdot}8$, as above, and substituting in expression (7)—the terms being continued until negligibly small—we have

$$\text{total m.m.f.} = 9{\cdot}2526laB_m. \quad . \quad . \quad . \quad . \quad (8)$$

Comparison of (6) and (8) shows that, at the above values of leakage and of flux density, the m.m.f. corresponding to the mean flux density is 0·39 per cent. less than that calculated for a parabolic variation of the leakage flux.

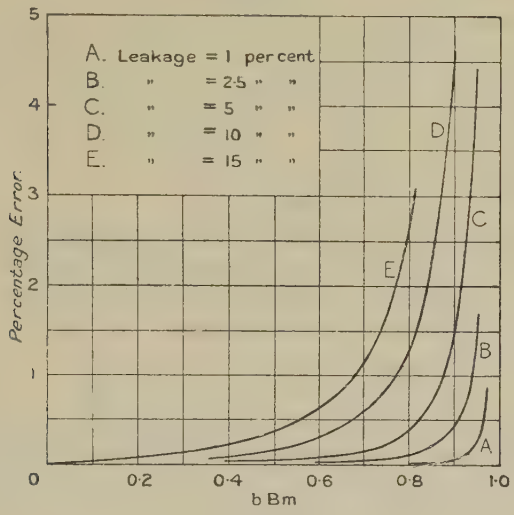
The difference between the m.m.f.'s derived from expressions (5) and (7) has been calculated as a percentage of the latter m.m.f. for different values of s and bB_m, and the results are given in fig. 13.

Since the curves of actual leakage flux (figs. 4 and 7) are intermediate between those assumed for deriving figs. 11 and 13, it is evident from these figures that, by winding the search-coil over the length of bar under test, the error involved in the measurement of m.m.f. is less than 1 per cent., except at very high values of the flux density and of the magnetic leakage.

It may be added that, with parabolic variation of leakage

flux and the above value of bB_m, the m.m.f. corresponding to B_m—namely, the flux density measured with a narrow search-coil—is 8·1 per cent. greater than the actual m.m.f. given by expression (8).

Fig. 13.



Conclusions.

(1) With the double bar and yoke method of magnetic testing arranged so that two symmetrical points on the specimen under test may be adjusted to be at the same magnetic potential, the flux density is a maximum midway along the specimen; and the magnetic leakage increases more rapidly than the distance from the centre, but less rapidly than the square of that distance.

(2) The magnitude and the variation of the magnetic leakage depend upon the permeabilities of the bar and of the yoke.

(3) With this type of tester, the distribution of the flux along the specimen is practically independent of the distribution of the magnetizing coil on the second bar and on the yoke, but is greatly affected by the length of the magnetizing coil on the specimen.

(4) With the apparatus shown in fig. 1, the magnetic leakage over the length for which the m.m.f. is determined has an average value of about 0·5 per cent. for mild steel when tested over a wide range of magnetizing force. For

cobalt-chrome steel, the corresponding value is about 4 per cent.

(5) By winding the search-coil over the length under test, the error due to magnetic leakage can be reduced to an extremely small value — even with comparatively large leakage ; and, since magnetic leakage cannot be entirely eliminated in bar tests, the search-coil should always extend over the length for which the m.m.f. is being determined.

(6) Above a certain percentage of the saturation density—depending upon the percentage leakage—the error due to magnetic leakage increases rapidly ; but such values of flux density require very high magnetizing forces and are seldom attained in magnetic testing.

The author desires to express his thanks to the Principal and the Governors of the Municipal Technical College, Brighton, for facilities to carry out the experimental work described in this paper.

XIII. *The Effect of a Magnetic Field on the Electrical Resistance of Mercury and some Amalgams.* *By* PHYLLIS JONES, *B.Sc.*, *and* T. J. JONES, *M.Sc.* (*Research Students, University College of Swansea*)*.

INTRODUCTION.

THE effect of a transverse magnetic field on the electrical resistance of mercury has been examined by Drude and Nernst †, Berndt ‡, Rossi §, and Nielson ‖. All the above observers obtained small increases of resistance due to the magnetic field, but Berndt noticed that the increase of resistance was less, the smaller the diameter of the tube. He found that for a field of three kilogauss, and a column of 0·29 mm. diameter, the change of resistance was less than 0·00005 per cent. Rossi investigated the change of resistance in mercury and in bismuth amalgams, and found that the change of resistance increased with the field, the diameter of the column, and the concentration of the amalgam.

Berndt came to the conclusion that if there were true magneto-resistance effects in mercury, they must be small

* Communicated by Prof. E. J. Evans, D.Sc., University College of Swansea.

† Drude and Nernst, *Wied. Ann.* xlii (1891).

‡ G Berndt, *Ann. d. Phys.* xxiii. (1907).

§ R. Rossi, *Nuov. Gim.* (6), ii. (1911).

‖ Nielson, Phys. Rev. p. 302, Feb. 1924.

compared with those obtained in the case of solid metals. This conclusion is confirmed by the work of Nielson, who used very fine tubes, and found an increase of resistance of 0·0003 per cent. for a magnetic field of sixteen kilogauss.

Recently two papers dealing with the problem have been published: one, mainly theoretical, by Williams *, and the other, containing the results of experimental work, by Jones †.

Williams, in his paper, assumes that the change of resistance of a column of mercury under the action of a transverse magnetic field is due to the two following causes :—

(i.) A change of resistance analogous to that observed in a solid metal (*i. e.* a true effect).

(ii.) A change of resistance, due to the development by the mechanical action of the magnetic field on the current, of mass motion of the mercury.

The first effect is proportional to the resistance r in the field, and the change of resistance due to this effect alone may, for a given field, be expressed by $\delta r_1 = Ar$, A being a constant for that field. The experiments carried out by Nielson show that for a field as large as sixteen kilogauss, A cannot be greater than 3×10^{-6}.

In the theoretical consideration of the second effect the motion of the mercury is regarded as being completely determined by the mechanical force "hi" (where "h" is the intensity of the magnetic field and "i" the current), the viscosity η, the density ρ, and the scale s, which is a measure of the various lengths involved in the system.

Dimensional analysis then gives for the change of resistance δr_2 arising from the motion of the mercury the general relation

$$\delta r_2 = \mathrm{B}\frac{h^2 s}{\eta} f\left(\frac{\eta^2}{his\rho}\right)\phi\left(\frac{\sigma}{\sigma'}\right), \quad . \quad . \quad . \quad . \quad (1)$$

where f and ϕ are any functions, B a numerical constant, and σ/σ' the ratio of the resistivity of the leads to that of the mercury. If the leads are sufficiently far removed from the field, the term $\phi\ (\sigma/\sigma')$ is a constant which can be included in B, and hence the total increase of resistance is

$$\delta \mathrm{R} = \delta r_1 + \delta r_2 = Ar + \mathrm{B}\frac{h^2 s}{\eta} f\left(\frac{\eta^2}{his\rho}\right). \quad . \quad . \quad (2)$$

* E. J. Williams, Phil. Mag. July 1925, pp. 27–46.
† T. J. Jones, Phil. Mag. July 1925, pp. 46–60.

It has been shown that if the motion of the mercury is steady, equation (2) reduces to

$$\delta R = Ar + B\frac{h^2 s}{\eta}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

However, if the motion of the mercury is turbulent, the change of resistance depends on the magnitude of the current, and is given by

$$\delta R = Ar + B\frac{h^{1+y} s^y}{i^{1-y}\eta^{2y-1}\rho^{1-y}}. \quad . \quad . \quad . \quad (4)$$

This formula can be simplified in the case of straight cylindrical tubes of diameter d, and assumes the form

$$\delta R = Ar + B\frac{h^{1+y} d^{y+\beta}}{i^{1+y}\eta^{2y-1}\rho^{1-y} t^{\beta}}, \quad . \quad . \quad . \quad (5)$$

where t represents the distance apart of the pole pieces and y and β are constants.

Jones * showed from his experiments that the comparatively large increase of resistance obtained in his experiments could be regarded as being altogether due to the turbulent motion set up in the mercury by the magnetic field, and that the value of y in equations (4) and (5) is 0·59. He also found for straight cylindrical columns that equation (5) could be written as

$$\delta R = B\frac{h^{1\cdot59} d}{i^{\cdot41}\eta^{\cdot18}\rho^{\cdot41} t^{\cdot41}}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

His experiments were carried out with straight tubes of diameters of about 0·5 cm. carrying currents varying from 0·5 to 5 amperes, and placed in a transverse magnetic field of two to ten kilogauss.

The present investigation was carried out to study the effects in tubes of smaller diameter and carrying smaller currents. It was hoped in this way to obtain the conditions necessary for steady motion, in order to verify, if possible, equation (3), in the case when the change of resistance is entirely due to motion,

$$i.e. \qquad \delta R = \delta r_2 = B\frac{h^2 s}{\eta}. \quad . \quad . \quad . \quad . \quad (7)$$

In this case the resistance should vary as the square of the field and inversely as the viscosity of the mercury.

* *Loc. cit.*

In this connexion Williams * examined the results obtained for mercury by Rossi, who used tubes of diameters 0·7 and 0·5 mm. and fields varying from 3350 to 4450 gauss. Williams showed that $\frac{\delta R}{h^2}$ was approximately constant; but since the current passing through the mercury column was not recorded, and also the variation in the magnitude of the field was small, the experiments were not satisfactory as a test of the theory.

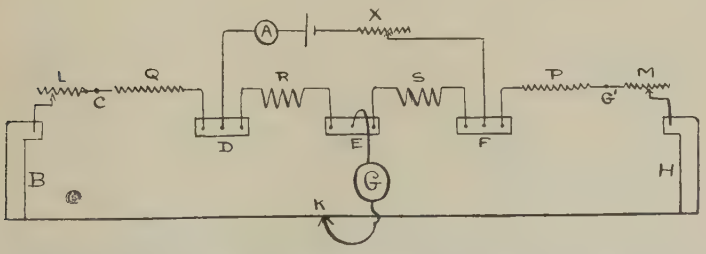
Rossi, as already stated, investigated the effect of a magnetic field on the resistance of bismuth amalgams, and found that the change of resistance increased as the concentration of the amalgam varied from 0·5 per cent. of bismuth to an amalgam saturated with the metal at 12° C. Williams, in his paper †, analyses Rossi's results, and on certain assumptions concludes that, in order to account for the experimental results, it is necessary to assume the existence of a true resistance change in bismuth amalgams.

It was therefore considered of some importance to examine the effect of a transverse magnetic field on the resistance of amalgams, and for this purpose amalgams containing 0·5 per cent. of bismuth and 1·187 per cent. of zinc were investigated.

Experimental Arrangement.

The Wheatstone bridge method was used to determine the changes of resistance produced by the magnetic field, and the connexions are shown in fig. 1.

Fig. 1.



R is the column of mercury which is placed in the magnetic field and is connected to the bridge by means of long flexible leads. S is a comparison column of mercury of nearly the

* *Loc. cit.* p. 35.
† *Loc. cit.* pp. 36–38.

same dimensions and resistance as R, and is connected to the bridge by flexible leads running close to those joining R to the bridge. The resistance S is out of the influence of the field, and the copper leads immersed in the mercury are for each tube out of the magnetic field. The resistances R and S, when the mercury was contained in bent tubes, were both immersed in a copper bath containing water, but when the columns were straight, variations of temperature were avoided as far as possible by surrounding the tubes with cotton-wool. The resistances P and Q between F and G′ and C and D respectively were 10-ohm manganin resistance coils, and were placed together in the same enclosure. M and L are also manganin resistance coils which could be varied in order to maintain a balance on the bridge wire joining B and H. The bridge wire was made of manganin, and had a resistance of 10^{-4} ohm per cm. The source of E.M.F. was a battery consisting of one or two storage cells and the current passing into the bridge system could be varied by means of a resistance X, and was measured by a Weston ammeter (A).

A sensitive Moll galvanometer (G) was employed to determine the change of resistance due to the magnetic field. Its zero was found to be very constant, and a microvolt applied to its terminals produced a deflexion of 6·46 mm. when the scale was at a distance of 162 cm. It had a period of about 1·5 seconds, and this quickness of action was found very useful in experiments of this type, where the conditions are continually changing and the increases of resistance to be measured are comparatively small.

The magnetic fields were obtained by means of a large circular electromagnet having pole-pieces 8 cm. in diameter at a distance apart of 1·65 cm. The fields used in the present experiments varied from 3000 gauss to 10,000 gauss, and were measured with a Grassot fluxmeter. The magnetic fields corresponding to known magnetizing currents were measured from time to time and found to be constant.

Two types of glass tubes, as shown in figs. 2 and 3, were used in the present experiments. In some cases it was only necessary to keep the tube in position, and investigate the effect of varying one of the quantities involved, such as the intensity of the field, on the increase of resistance. In other cases it was necessary to remove the tube and replace it in exactly the same position.

The magnitude of the effect depends upon the position of the tube with respect to the magnetic field, and consequently the method of mounting the tubes was so designed as to

Fig. 2.

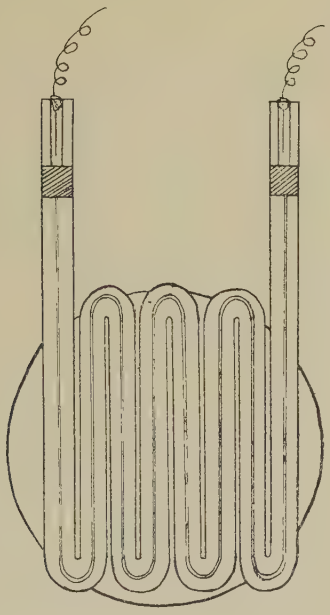
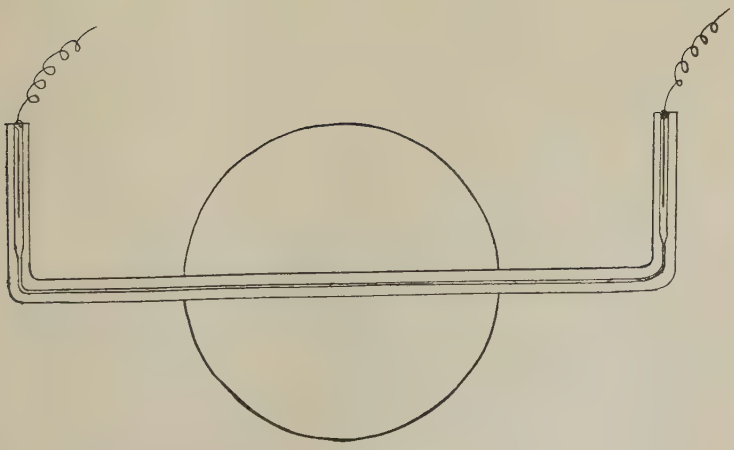


Fig. 3.



make it possible to replace the tube in exactly the same position when necessary. The changes of resistance were determined as follows :—

The bridge was first balanced when the magnet was not excited, and the position of the fine line in the image of the spot of light on the scale was noted. The magnetizing circuit was then closed and the new position of the spot of light noted. Finally, the magnet circuit was broken and zero position again noted. The difference between the mean of the first and third readings and the second was taken as the deflexion produced by the magnetic field. Sometimes the mode of procedure was varied, and the bridge was first balanced with the magnetic field on, and the deflexion produced on breaking the magnetic circuit measured in a similar manner.

The deflexions measured in this investigation varied from about 2 mm. to about 12 cm., depending upon the intensity of the magnetic field and the magnitude of the current passing through the mercury column. The definition of the light-spot was so good that the position of the line could be estimated to 1/10th of a mm. When the current passing through the mercury was small, and the temperature of the column approximately that of the room, the difference between the two zero readings (the first and third mentioned above) was small, and in a large number of cases the two readings were identical. When, however, the currents sent through the mercury were of the order of 1 ampere, the Joule heating-effects and, to a smaller extent, the heat produced by the magnet caused trouble, and the difference between the two zeros was appreciable. It was found possible to take satisfactory readings in this case, and only observations in which the difference between the first and third readings was small in comparison with the total deflexion, were finally considered.

When investigating the effect of temperature (or viscosity) on the change of resistance, the spot of light was found to be a little unsteady and the values of the deflexions were not as constant as in the experiments carried out at room temperatures. In these experiments the outside limbs of the bent tube were out of the heating bath, and the unsteadiness was probably caused by thermoelectric currents, due to slight temperature differences in the two mercury tubes. The effect was diminished by wrapping the limbs with asbestos cord.

From the magnitudes of the deflexions, knowing the sensitivity of the galvanometer and the magnitude of

the current entering the bridge whose resistances were also known, it is possible from the well-known Wheatstone bridge equations to calculate the change of resistance produced in the mercury by the magnetic field. Since the change of resistance in these experiments is small, and of the order of 10^{-5} ohm, the deflexion due to it is proportional to the product of the change of resistance and the current passing through the mercury resistance in the field.

When the deflexions are about 1 cm. or more, and the experiments are carried out in tubes of diameter 1·1 mm. under ordinary circumstances at room temperature and using currents between ·03 and ·5 amp., it is considered that the results are correct to within 3 or 4 per cent. The results obtained with narrow tubes of diameter about 0·5 mm. are not as accurate, and only small currents were used, owing to the heating effect of the current and the difficulties caused by air-bubbles. The variation of temperature during the course of a set of experiments was not greater than about 5° C., and during the whole period of experimenting the temperature only varied from about 9° C. to about 17° C. The changes in the value of δR, due to a change of temperature of this amount, are within the experimental error involved in the determination of δR.

In this investigation, as was also shown previously by Jones *, the increase of resistance observed is not related to the magnitude of the resistance in the field. The effect is probably produced by motion set up in the mercury at points in the tube, where either the magnetic intensity or the current density changes in value, and consequently a change in the position of the tube (especially the bent tube) will cause an appreciable change in the value of δR.

In the present experiments the resistance in the field was about 87 per cent. of the total resistance of the mercury column for the bent tube, and varied from about 30 per cent. to 40 per cent. in the case of straight tubes.

Experimental Results.

The Variation of δR for mercury with the current "i" and the magnetic field "h."

Experiments were carried out with bent tubes of diameters 1·1 mm. and 0·4 mm. and with a straight tube of diameter

* *Loc. cit.*

0·96 mm. In the case of the bent tube of 0·4 mm. diameter, experiments were carried out for small currents only, as the Joule heating effect made accurate observations impossible for currents of the order of 0·3 ampere. The experimental results are given in Tables I., II., and III.

Table I.

Bent tube of diameter 1·1 mm.
Resistance of mercury column in field = 0·64 ohm.
Total resistance of mercury column = 0·76 ohm.

h in gauss.	$\delta R \times 10^6$ ohms for currents ranging from ·03 to 1·4 amperes.									
	·03	·047	·065	·14	·338	·476	·772	1·144	1·256	1·395
10,000...	56·4	56·52	56·57	54·66	47·69	43·59	37·84	33·9	32·8	31·52
9,000...	45·38	45·93	45·76							
8,150...	37·1									
7,750...	...	...	36·63							
7,071...	...	...	28·29	...	25·78	...	...	...	...	18
6,500...	...	24·12								
6,000...	...	...	20·42							
4,814...	...	...	13·01	...	12·89	...	...	...	...	9·696
4,101...	...	...	9·36							
3,198...	...	...	5·657							

Table II.

Bent tube of diameter 0·4 mm.
Resistance of mercury in the field = 4·89 ohms.
Total resistance of mercury column = 5·38 ohms.

h in gauss.	$\delta R \times 10^6$ ohms for currents of ·039 and ·078 ampere.	
	·039	·078
10,000	24·36	22·04
7,071	11·06	11·94

TABLE III.

Straight tube of diameter 0·96 mm.
Resistance of mercury column in field = ·106 ohm.
Total resistance of mercury column = ·36 ohm.

h in gauss.	$\delta R \times 10^6$ ohms for currents ranging from ·068 to ·58 ampere.					
	·068	·097	·145	·29	·386	·58
10,000.....	28·84	27·653	26·228	22·81	20·14	16·93
7,071.....	14·62	13·828	13·59	...	11·76	
4,814.....	...	6·049	...	...	6·518	

Variation of δR *with the Current "* i*."*

If the results collected in Table I. (bent tube of diameter 1·1 mm.) are examined, it is evident that for currents of ·03, ·047, ·065 ampere, the value of δR is independent of the current. As the magnitude of the current increases, the value of δR diminishes, and if, for a constant field, $\delta R \propto \frac{1}{i^x}$, the value of the index "x" for two given currents can be determined from the experimental results. If, for instance, the values of δR for currents of ·338 and ·476 ampere and a field of 10,000 gauss are taken, the value of "x" is found to be ·26. The value of "x" calculated from two currents increases as the magnitudes of the currents increase, until it becomes ·37 for currents of 1·144 and 1·395 amperes. Unfortunately, larger currents could not be passed through the tube, owing to experimental difficulties caused by the Joule heating effect.

Similar results are obtained if Table III., which gives the results with a straight tube, is examined.

For currents of ·068 and ·097 ampere the value of δR for a given field is, within experimental error, independent of the current. As the current increases, the value of δR corresponding to a given field (10,000 gauss) diminishes, and the index "x" increases until it reaches an almost constant value. The value of "x" for currents of ·145 and ·29 ampere

and a field of 10,000 gauss is ·2, and for currents of ·29, ·386, and ·58 ampere, taken in pairs, assumes an approximately constant value of ·43.

Jones had previously shown for large currents in wide tubes that, for a constant value of the field, $\delta R \propto \frac{1}{i^{\cdot 42}}$, a result in agreement with Williams's theory, if the magnetic field produces turbulent motion in the mercury.

In the present experiments it has been shown that, for narrower tubes and smaller currents, δR is independent of the current. This result is also in agreement with Williams's theory, if the mercury is in steady motion. Furthermore, it is seen that as the current passing through the mercury increases, the value of "x" increases from 0 to 0·43, which is practically the same value as obtained by Jones.

The Variation of δR *with* "h."

In order to consider the variation of δR with the field for a constant current, Tables IV. and V. have been constructed from the results collected in Tables I. and III.

TABLE IV.

Bent tube of diameter 1·1 mm.

"h" in gauss.	$\frac{\delta R}{h^2} \times 10^{14}$.		$\frac{\delta R}{h^{1\cdot 79}} \times 10^{13}$.	$\frac{\delta R}{h^{1\cdot 61}} \times 10^{12}$.
	·03 amp.	·065 amp.	·338 amp.	1·395 amps.
10,000	56·4	56·57	32·993	11·45
9,000	56·02	56·49		
8,150	55·85			
7,750	...	55·99		
7,071	...	56·58	33·159	11·41
6,000	...	56·72		
4,814	...	56·13	33·009	11·42
4,101	...	55·65		
3,198	...	55·31		

TABLE V.

Straight tube of diameter 0·96 mm.

"h" in gauss.	$\frac{\delta R}{h} \times 10^{14}$.		$\frac{\delta R}{h^{1\cdot54}} \times 10^{12}$.
	·068 amps.	·097 amp.	·386 amp.
10,000	28·84	27·656	13·93
7,071	29·24	27·66	13·87
4,814	...	26·10	13·897

From these tables it follows that, for low values of the current, δR is proportional to h^2 for both the bent and straight tubes. This result is in agreement with Williams's theory when the mercury is in steady motion. As the current increases, $\delta R \propto h^x$, where "x" assumes values smaller than 2. In the case of the bent tube, the smallest value reached by "x" is about 1·61, which is not far removed from the constant value 1·58 obtained by Jones for large currents passing through mercury contained in wider tubes. In the case of the straight tube the smallest value of "x" was 1·54, which, again, is in fairly good agreement with Jones's value.

The experimental results collected in Tables I. and III. show that, for small currents passing through mercury contained in tubes of diameter about 1 mm., $\delta R \propto h^2$, and is independent of the current. As the current increases, δR becomes dependent on the current, until finally $\delta R \propto \frac{h^{1\cdot57}}{i^{\cdot43}}$. The latter result was first obtained by Jones, and both results support the theory put forward by Williams.

The experiments with a narrow tube of diameter 0·4 mm. were carried out to determine the value of $\frac{\delta R}{R}$ for a given value of "h" when a large resistance was placed in the magnetic field. The results of other observers, in the case of mercury, have often been given in this form, but Jones, in the case of wide tubes, had shown that δR does not depend on the resistance in the field.

A comparison of the results obtained with the two tubes for a given field shows that δR is less for the tube of the smaller diameter, although the resistance in the field is 7·6

times greater than for the tube of large diameter. The result supports the view that the increase of resistance is due to motion set up in the mercury. The two tubes were not similar, as the one of smaller diameter had more bends in it than the other. The results cannot, therefore, be employed to study the effect of diameter on the increase of resistance of δR. The results with this tube are not as accurate as those obtained with the tube of larger diameter, as the deflexions measured were small. For instance, the deflexion measured for a current of ·08 ampere for a field of 7071 gauss was only 1·26 mm.

The value of $\frac{\delta R}{R}$ for a field of 10,000 gauss and a current of ·04 ampere is $4{\cdot}1 \times 10^{-6}$ ohm, and the motion in this case is probably steady.

Variation of δR *with Temperature.*

These experiments were carried out to determine the change in the value of δR with rise of temperature of the mercury. Jones* had previously shown that the increase of resistance $\delta R \propto \frac{1}{\eta^{\cdot 18}}$ in the case of wide tubes carrying large currents. A relation of this type is to be expected on Williams's theory, if the motion of the mercury is turbulent. If, however, the motion is steady, the increase of resistance should vary inversely as the viscosity η.

Experiments were, therefore, carried out on mercury contained in a bent tube of diameter 1·1 mm., carrying a current of ·065 ampere and placed in a magnetic field of 10,000 gauss. The change in resistance δR was measured at room temperature, the temperature of boiling water, and the temperature of boiling aniline. In order to get rid of air-bubbles, the tubes containing the mercury were heated to temperatures higher than those used in the present experiments, and the mercury sucked through the tubes in both directions. The deflexions observed were slightly variable, but it is hoped that the mean values are correct to within about 8 per cent. These experiments will again be repeated under more satisfactory conditions.

The value of δR was re-determined at room temperature after heating to a higher temperature, and found to be the same as the initial value within experimental error. The

* *Loc. cit.*

expansion of the glass, due to the rise of temperature, has no appreciable effect on the magnitude of the current passing through the tubes, and the change of diameter of the tube can be neglected when considering the variation of δR with the viscosity η. The bent tube, which was placed in the magnetic field when experiments were carried out at the temperature of boiling water, was replaced by the other bent tube when experiments were carried out at the temperature of boiling aniline. The deflexions obtained at the various temperatures are given in Table VI.

TABLE VI.

Temp. of Mercury 15° C. Deflexion in mm.	Temp. of Mercury 99° C. Deflexion in mm.	Temp. of Mercury 15° C. Deflexion in mm.	Temp. of Mercury 180° C. Deflexion in mm.
10·5	14·5	11·3	19·0
10·5	13·5	11·6	17·3
10·5	14·5	11·6	16·3
10·5	14·3	—	17·3
10·7	14·2	—	16·3
—	12·6	—	19·0
—	12·9	—	16·5
—	14·8	—	—
—	13·8	—	—
—	12·6	—	—
—	13·0	—	—
Mean 10·54	Mean 13·7	Mean 11·5	Mean 17·4

According to the above table, $\frac{\delta R_{99° C.}}{\delta R_{15° C.}} = 1{\cdot}3$

and $\frac{\delta R_{180° C.}}{\delta R_{15° C.}} = 1{\cdot}51.$

The approximate values* of $\frac{\eta_{15° C.}}{\eta_{99° C.}}$ and $\frac{\eta_{15° C.}}{\eta_{180° C.}}$ are 1·3 and 1·51 respectively.

It is therefore concluded, within the limits of experimental error, that δR varies inversely as the viscosity. This is the result to be expected if the motion set up in the tube is steady.

* Kaye & Laby's Tables of Physical Constants, p. 30.

Experiments carried out with two straight tubes of different diameters.

Two tubes of diameter ·96 and ·5 mm. respectively were placed in almost exactly the same position with respect to the magnetic field, and the values of the deflexions for each tube determined for a current ·066 ampere and a field of 10,000 gauss. The resistances of the two tubes were ·36 and ·99 ohm, and their lengths 27 and 20 cm. respectively. The leads were out of the field, and, as previously shown by Jones *, the effect for straight tubes is independent of the resistance in the field. The experiments were carried out under conditions of steady motion $\left(\frac{\delta R}{h^2} = \text{constant}\right)$, and it was found impossible to obtain reasonably accurate results with tubes of smaller diameter than ·5 mm., as the deflexions obtained were too small. Jones † had previously investigated the effect of varying the diameter in the case of wide tubes carrying large currents $\left(\frac{\delta R}{h^{1\cdot58}} = \text{constant}\right)$, and found that δR was proportional to the diameter. The results obtained for the two tubes are given below in Table VII.

Table VII.

Current in amperes.	Field in gauss.	Tube of diam. ·96 mm. $\delta R \times 10^6$ ohms.	Tube of diam. ·5 mm. $\delta R \times 10^6$ ohms.
·066	10,000	24·19	12·24

The results show that δR increases with the diameter of the tube, and that it varies approximately as the diameter of the tube.

The Effect of a Magnetic Field on the Resistance of Amalgams.

In the first series of experiments the increase of resistance produced in pure mercury was compared with the increase produced in an amalgam containing 0·5 per cent. of bismuth.

Bent tubes were employed in these experiments, and after

* *Loc cit.* † *Loc. cit.*

measurements had been made for pure mercury, the tubes were filled with the amalgam and replaced in exactly the same position. After the observations had been completed in the case of the amalgams, the tubes were again filled with pure mercury and the first set of measurements were repeated. Experiments of a similar kind were carried out with straight tubes filled with pure mercury, an amalgam containing 0·64 per cent. of bismuth, and an amalgam containing 1·187 per cent. of zinc. The results obtained are given in Tables VIII. and IX.

Table VIII.

Bent tube of diameter 1·1 mm. containing Mercury and Bismuth amalgams.

Field h in gauss.	Pure Mercury.			Amalgam containing 0·5 per cent. Bismuth.		
	Deflexion in mm.			Deflexion in mm.		
	·065 amp.	·13 amp.	·465 amp.	·065 amp.	·13 amp.	·465 amp.
10,000	10·75	21·8	61·2	10·55	21·1	60·4
7,904	...	13·6	...	...	13·75	41·35
7,071	5·25	10·9	...	5·3	11·35	32
4,814	2·42	5·2	...	2·5	5·15	14·9

Table IX.

Straight tube of diameter ·96 mm. containing pure Mercury, Bismuth amalgam, and Zinc amalgam.

Currents in amperes.	Field in gauss.	Pure Mercury. Deflexion in mm.	Amalgam containing ·646 per cent. of Bismuth. Deflexion in mm.	Amalgam containing 1·187 per cent. of Zinc. Deflexion in mm.
·068	10,000	4·9	4·76	4·59
·279	10,000	17·5	17·2	16·7

These experiments show that, within the limits of experimental error, there is no appreciable difference between the increase of resistance in the case of pure mercury and the amalgams examined. If the effect measured is due entirely to the motion of the liquids, the increase of resistance should be less in amalgams than in pure mercury, owing to the increase of viscosity produced by solution of a metal in mercury. According to the measurements of Feninger *, the viscosity of 0·64 per cent. bismuth amalgam is 1·08 per cent. greater than that of pure mercury. It therefore follows that the deflexion for small currents (·068 ampere) when the motion is steady should be 1·08 per cent. less than for pure mercury, and the difference should become less for higher currents when the motion is turbulent. The difference due to change of viscosity is, however, too small to be measured with accuracy for the bismuth amalgams of the concentrations employed in the present experiments. The viscosity of 1·187 per cent. zinc amalgam † is 6·54 per cent. greater than that of pure mercury, and the deflexions obtained for small currents should be 6·54 per cent. less than for pure mercury. The evidence seems to indicate that there is a small diminution in the increase of resistance produced by the field when bismuth and zinc are dissolved in mercury. The experiments support the view that the increase of resistance produced in amalgams by a transverse magnetic field is due to motion produced in the amalgams ; and the results are not of sufficient accuracy to decide if the solution of bismuth or zinc in mercury produces a very small real effect of the same type as observed in solid metals. A very small effect of this kind may possibly be superimposed on the much larger effect due to motion.

Experiments with flat glass cells of rectangular cross-section.

Some experiments were carried out on the increase of resistance produced in mercury contained in flat glass cells of rectangular cross-section. When the depth of the cell is large compared with its width, the effect seems to be more complicated than for tubes of circular cross-section. If the depth of the cell is made equal to its width, so that the cross-section of the mercury column is a square, the laws followed

* Feninger, "Die Elektrische Leitfähigkeit und innere Reibung verdünnter amalgame." Inaugural Dissertation, Freiburg, 1914

† Feninger, *loc. cit.*

by mercury when contained in a tube of circular cross-section are obeyed.

Further experiments will be carried out on this problem.

Summary of Results.

1. Experiments were carried out on the increase of resistance of mercury contained in bent and straight tubes for values of the current ranging from ·03 to 1·4 amps., and for fields ranging from 3,000 to 10,000 gauss.

2. It was found for tubes having diameter of about 1 mm., and for small currents, that the increase of resistance is independent of the current passing through the tubes, and is proportional to h^2.

3. As the magnitude of the current passing through the mercury increased, the change of resistance δR became dependent on the current until finally (for the maximum current employed in these experiments)

$$\delta R \propto \frac{h^{1\cdot58}}{i^{\cdot4}}.$$

4. The effect of temperature on the change of resistance was also investigated, and it was found that the increase of resistance for small values of the current varied inversely as the viscosity.

5. The results obtained are in agreement with a theory put forward by Williams, who assumes that the increase of resistance is due to the production of motion in the mercury and amalgams by the action of the magnetic field.

6. The increase of resistance was examined for two straight tubes of diameter ·96 and ·5 mm. respectively, and it was found to be approximately proportional to the diameter for small values of the current passing through the mercury column.

7. The increase of resistance produced in amalgams containing 0·5 and 0·64 per cent. of bismuth and an amalgam containing 1·187 per cent. of zinc was measured, and it was concluded for the concentrations employed that the solution of either bismuth or zinc in mercury produced no appreciable change in the increase of resistance. The experiments showed a slight diminution in the change of resistance produced by the magnetic field when bismuth and zinc are dissolved in the mercury. This result is to be expected on the theory that in conducting liquids the

increase of resistance is not a true effect, but is produced by the motion set up in the liquid.

This motion is less in amalgams than in pure mercury, as the viscosity of the former is greater.

These experiments were carried out in the physics laboratories of the University College of Swansea under the guidance of Professor E. J. Evans, and we thank him for his valuable suggestions and constant advice.

We also thank the Department of Scientific and Industrial Research and the Glamorgan County Council for grants which made this research possible.

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XIV. *The Analysis of the Copper Spectrum.*

By W. M. Hicks, *F.R.S.**

I. The Linkage Systems and the Rydberg Separations.

ALTHOUGH the existence of links was first made evident during a discussion of the copper spectrum, the linkages of Cu have not hitherto been considered in detail. The present communication is confined to the discussion of these linkages and includes an attempt to fix the origin and the nature of the Rydberg separations †. It is hoped in a later paper to deal with certain aspects of the series relationships, especially in the light of two recent important papers by Shenstone ‡ and by Stücklen §.

1. It should be remembered that every link enters as the difference of two comparatively near term levels. We may indeed imagine that in the violence of the spark excitation a recombining electron may give some of its excess energy to the other electrons round the nucleus. We may picture the process as first a set of shocks to each electron or some of them round the nucleus, displacing them and altering

* Communicated by the Author.

† I have been criticised because in my various papers on the analysis of spectra I do not refer to the generally accepted views as to the detailed way in which the electrons outside the nucleus are arranged or move. But my aim has been not to illustrate a theory—or to criticise it—but to examine the spectral data themselves and try to discover their interrelations and the laws on which they are built up. Many of these are of great simplicity, and they ought to be taken account of by those specially working on general theory.

‡ Phil. Mag. xlix. p. 951 (1925).

§ *Zeit. f. Phys.* xxxiv. p. 562 (1925).

their energies. But the new configurations may not be those governed by quantum considerations. Consequently in their accelerations they dissipate a portion of their energies until they fall into a quantum configuration (*i. e.*, a non-dissipating one) near their original paths. Next they fall into their original states and pass on their freed energy to the nucleus to be radiated according to quantum laws. The different levels in each case may be those of a complex term (different j, same k) or in general may be certain others not usually occupied in the normal or quiet transitions, but which we can calculate with very great exactness so soon as we know the usual series limits and separations. Again, when one level, or the two levels, of a quietly transiding electron is modified we get displaced lines. Such for instance are the origins of the various series and satellite separations which may be called normal displacements. Summation lines (almost wholly spark lines) must have a completely different origin. Until we know their source we may provisionally suppose that they are due to the existence of a doubly ionized atom simultaneously neutralized by two electrons, one going to the limit term level and the other stopping momentarily at a higher term level. *E. g.*, we might suppose $\mathbf{S}(3)$ or $p(1)+s(3)$ to be due to the presence of the $++$ atom simultaneously neutralized by one electron falling in to the $p(1)$ level and the other to $s(3)$. Naturally in all these cases simultaneity would never happen, and we should have to imagine that some short interval is required in settling down *or* that there is some short interval between the complete transmission of energy from the electrons to the nucleus and its emission as radiation by the latter.

The existence of linked lines shows that the general supposition that all spectral lines are due to the difference of two terms only is too restricted. Many such in the long lists of new terms in elements which have been published by several investigators lately possibly contain many spurious ones due to this belief. Even negative terms have been admitted which should correspond to impossible * finite orbits whose total energy is greater than that from infinity. For instance, in the summation example above of $\mathbf{S}(3)$ the second term would be regarded as a negative one. But such an explanation is merely verbal and can correspond to no reality. The idea that a line might be represented as the sum or difference of the frequencies of two other lines

* That is, if any magnetic action of the nucleus is neglected, as is usually done in current theory.

(*i. e.* dependent on four terms) is not a new one. Moggendorff * indeed attempted to give examples of such, although unfortunately all his instances reduced † in reality to the difference of two terms only.

2. For data we have very accurate measures between 8680 and 6740 by Meggers ‡. He gives estimates of his probable errors varying from ·01 to ·05. Below 6740 the measures of Hasbach § are used except that in the region down to 5000, where he has observed comparatively few lines, the observations of Aretz ‖ are used and in the sparse region of arc lines from 5700 to 5000 spark lines, chiefly by Eder and Valenta ¶, have been taken into consideration. Exner and Haschek ** have also noted many extra arc lines, some of which have been made use of. The original observations of Kayser and Runge are now replaced by the very accurate ones of Hasbach, working in Kayser's laboratory. He reads to three places of decimals in the majority of his lines, and in *general* his observation errors may be taken as not greater than a few units in the last place. That this is so may be inferred by comparison with other observers, who in special cases have observed single Cu lines also to three places. Some examples are given below in connexion with his complex lines. Aretz also observes to three places, but for reasons given by Hasbach they are often in error by one or two units in the second place. His separations of near lines, however, are not affected to the same degree.

The Satelloid Group.

3. Hasbach gives a considerable number of strong lines as complex, exhibiting numerous companions ("trabanten"). The laws of the separations of the companions of complex lines are little known. The separations are generally small and do not depend like the series separations on oun displacements. The separations of Hasbach's lines are larger than those of complex lines in general. Janicki gives only four lines as complex, viz. the two inverse D'_{12}, D'_{22} lines where Hasbach has none and the other two in common with him, but with smaller separations. We might almost suspect them to be the result of a Stark effect were it not for their

* *Proc Kon. Akad. Wet ns. Amsterdam*, Dec. 1911.
† 'Analysis of Spectra,' p. 37.
‡ Bull. Bureau Stand. Wash. No. 312 (1918).
§ *Zs. wiss. Phot.* xiii. p. 399 (1914).
‖ *Zs. wiss. Phot.* ix. p. 256 (1910).
¶ *Denks. Wien. Akad.* lxiii. p. 189 (1896): data taken from Kayser, Bd. 5. Referred to as E.V.
** *Spek. der El. bei normalem Druck*, 1911, 1912. Referred to as E.H.

irregularity and the fact that none of them appear in D lines. So also the irregularity of the spacings and the fact that near lines of the same character do not show them would seem to exclude the supposition that they are due to ghosts; *e. g.*, whereas (4) 3208, (6) 3194 show them, the near lines (4) 3231; (6) 3142; (6) 3126 do not. Moreover, the linkage maps, as we shall see, show that they belong to one related system—a strong indication that their source must be looked for in term properties and not in grating deficiencies. They are not satellites as ordinarily understood, and I shall refer to them as satelloids. They show certain peculiarities which are important for our present purpose as well as for their experimental illustration of known link properties. They deserve a preliminary discussion. Quite recently Stücklen * has observed satellites, but more numerous, in the same lines. She does not, however, give measures and does not appear to be aware that Hasbach had already observed them. The whole set are given in the following list. The intensities are of the order 6 ± 2.

TABLE I.

	1 (5, VIII.).		
4704·598 [1]	21249·87		*y*
04·20	51·67	1·80	$3y=1·71$
	2 (7, VIII.).		
2·30	88·75	5·40	$9y=5·13$
1·986	90·20	3·95	$7y=3·99$
4651·130 [2]	21494·15		*y*
0·73	96·00	1·85	$3y=1·71$
0·3	97·98	3·83	$7y=3·99$
		9·23	$16y=9·12$
	3 (?)		
5·45	82·79	1·74	$3y=1·71$
4275·131 [3]	23384·53		? *y*
4·79	86·42	1·91	$3y=1·71$
	4 (51, VI.).		
3602·038	27754·18		*y*
01·75	56·39	2·21	$4y=2·28$
	5 (16, VI.).		
0·67	15·18	2·26	$4y=2·28$
0·55	16·14	1·30	
3530·388	28317·44		*y*
0·252	18·53	1·09	$2y=1·14$
0·10	19·75	2·31	$4y=2·28$
		5·57	$8y=5·56$
	6 (47, VI.).		
8·45	45·44	5·38	$10x=5·40$
8·11	48·49	2·33	$4y=2·28$
8·04	49·11	1·71	$3y=1·71$
3337·850	29950·82		*y*
7·73	51·90	1·07	$2x=1·08$
7·668	52·45	1·62	$3x=1·62$
7·571	53·32	2·50 [4]	
		7·88	$14y=7·98$
	7 (2, I.).		
8·55	16·06	5·45	$10x=5·40$
3307·952	30221·51		*x*

[1] Janicki gives triplet *dn* ·148; ·174.
[2] Janicki gives as single and very sharp.
[3] Have no attached links. Janicki gives doublet *dn* ·264.
[4] This is a $2\delta_1$ displacement on $p_1 = 2·47$. The total for the others is then 7·00 with $13x=7·02$; for more complete treatment see note 6 to Map VI.

* *Zsch. f. Phys.* xxxiv. p. 562 (1925).

TABLE I. (*continued*).

	8 (3, II.).		
3·09	50·36	3·48	$6y=3·42$
3282·716	30453·84		y
2·33	57·42	3·58	$6y=3·42$
	9 (6, I.).		
80·687	72·67	8·02	$15x=8·10$
80·40	75·34	5·35	$10x=5·40$
3279·823	30480·69		x
79·54	83·33	2·64	$5x=2·70$
79·06	87·78	7·09	$13x=7·02$
		15·11	$28x=15·12$
	10 (5, I.).		
3208·236	31160·80		y
8·119	61·93	1·13	$2y=1·14$
7·94	63·69	2·89	$5y=2·85$
7·65	66·50	5·70	$10y=5·70$
	11 (17, II.).		
4·66	93·23	5·44	$10x=5·40$
4·34	96·36	2·31	$4y=2·28$
3194·103	31298·67		x
3·979	99·89	1·22 [5]	
3·81	301·35	2·68	$5x=2·70$
		8·12	$15x=8·10$
	12 (8, I.).		
3108·603	32159·49		x
8·43	61·55	2·06	$4x=2·16$
	13 (4, III.).		
3093·993	32311·36		y
3·72	14·25	2·89	$5y=2·85$
	14 (5, III.).		
3073·803	32523·58		x
3·704	24·62	1·04	$2x=1·08$
3·53	26·35	2·77	$5x=2·70$
	15 (30, II.).		
3063·416 [6]	32633·84		x
3·18	36·35	2·51	$5x=2·70$
	16 (3, III.).		
3036·105	32927·38		y
5·89	29·72	2·34	$4y=2·28$
5·84	30·26	2·88	$5y=2·85$
	17 (notes to III.).		
2997·363 [7]	33352·97		x
7·13	55·57	2·60	$5x=2·70$
	18 (10, III.).		
1·76	54·38	6·15	$11y=6·27$
2961·177	33760·53		y
0·92	63·48	2·95	$5y=2·85$
		9·10	$16y=9·12$
	19 (?)		
3·18	73·78	2·92	$5y=2·85$
2882·937 [8]	34676·70		
2·713	79·40	2·70	$5y=2·85$
		5·62	$10y=5·70$

[5] This is one oun on p.

[6] Is Shenstone's $d_2'-p_f$.

[7] See note 4 to map III.

[8] Has no links—is Shenstone's $Y-p_f$.

The first column gives wave-lengths, the main line being in full; the second wave-number; the third and fourth are explained below. The brackets following the ordinal number refer to the maps in which the lines occur.

To illustrate the degree of accuracy of Hasbach's measures referred to above, the readings of other observers for some of the lines in the table are here appended.

	1.	3.	4.	5.	6.	7.	11.	16.	18.
Hasbach	·598	·131	·038	·383	·850	·952	·103	·105	·177
Offermann	·605	—	·035	·385	·851	·950	·106	·107	·186
Hamm	·597	·132	—	·390	·848	·950	...	·103	·180
Josewski.....	—	·136	·045	—	—	—	·108	—	—
Vahle	—	—	·037	—	—	—	—	—	—

A similar result obtains if the numerous other cases given in Kayser's *Handbuch* are examined. I find only one case of real deviation, in which for Hasbach's 2441·625 Hamm gives ·665, Krebs ·651, E.H. ·67, and Huppers ·67. The deviation is so excessive that we must take it as a printer's or MS. error and that his true reading is ·665. We may feel some certainty, therefore, that his observation errors are in general less than ·005 when he reads to ·001.

If we examine the separations of the satelloids from their main lines, we shall see that they are practically all multiples of one of the two quantities $x=·54$ or $y=·57$, and that this is specially marked if we consider the separations of the extreme satelloids. Compare for instance their values for (5, 6, 9, 10, 11, 16, 18, 19). The intermediate satelloids are in general in good agreement with this rule, but they show slight indications of small shifts of pairs such as might be explained by a small Stark effect. The close agreement, with the large multiples involved, is extraordinary and shows that the effect is real. This sense of reliability is increased if the cases where a satelloid is measured to ·001 are considered. This dependence on multiple shifts, now to be regarded as established, is important as a sure evidence that the satelloid sets are all due to displacements in some one term (or two, if x is really different from y). In other words, all the lines involved must contain some common term in their formulæ. This conclusion is supported, as we shall see below, by the linkages which definitely relate the majority of these satelloid sets to P (1) lines. They are also closely associated with the maps in which Rydberg's 680·11 and 212·23 occur. We may suspect, then, that all these lines should really depend on P (1). Amongst others (15, 19) would then suggest that Shenstone's p_f are composite terms involving $p_1(1)$ or $p_2(1)$. The origin of the y shift must remain at present undetermined. If the satelloids are of the same nature as that of the close companions of strong lines, we should not expect the shifts to be due to oun displacements on a single term, and indeed such small shifts could not be produced in either of the terms $s(1)$–$p(1)$. The oun shift on $s(1)$ is 3·43 which is $6y=3·42$, but this must be merely a curious coincidence for fractional ouns are inadmissible.

Stücklen has attempted to explain the satelloids as being of a band-like nature caused by the association of an atom with another very slightly bound one.

The existence of these satelloids is of extreme importance on another ground, in that they afford direct experimental

evidence for the link modifications. We already know that as a fact when two lines are linked, their separation often differs slightly from that of the actual link. A link attached to a line A will indicate a line close to B, but this line may not be observed, and in general we find, when the terms involved are known, that B is displaced from its theoretical value by definite displacements in these terms. The evidence for this effect is definite *. The interest of these sets of Hasbach's just lies in the fact that in very many cases the satelloids give these theoretical lines. The discussion is best deferred until the linkage maps have been considered and it is taken in § 8.

The Linkages.

4. In its linkage systems copper is anomalous in that linked lines are found in the arc spectrum itself and not, as in other spectra, only to spark lines. In silver and gold no links are found within the spectrum as produced in the arc, although of course the various chains start from series or other definite non-ionized atomic lines. The usual links for Cu as given in a previous communication † are, when corrected to IA,

$$a=245{\cdot}54\ ;\quad b=248{\cdot}44\ ;\quad c=251{\cdot}39\ ;\quad d=254{\cdot}39\ ;$$

$$e=999{\cdot}80\ ;\quad u=680{\cdot}63\ ;\quad v=692{\cdot}08.$$

These can only be indeterminate within one or two units in the last decimal. The $a \ldots d$ links in Cu differ so slightly that we shall make small use of them in the present discussion, chiefly because it is difficult to determine whether separations near their values are real links, or direct displacements, or pseudo-separations such as we get between D_{11} and D_{22} lines with near satellites not visible. Their existence, however, is evident on any preliminary testing of the spectrum, and they are the origin of the large number of separations near that of the doublets to which Rydberg ‡ first drew attention nearly thirty years ago. As is well known, he brought to light numerous sets of new separations about 680, 212, 130, and 50 for which he could give no explanation. We shall refer to the three latter categories as X, L, M. He arranged some of these (shown with thicker connecting lines in map VI.) in a peculiar form of multiplet

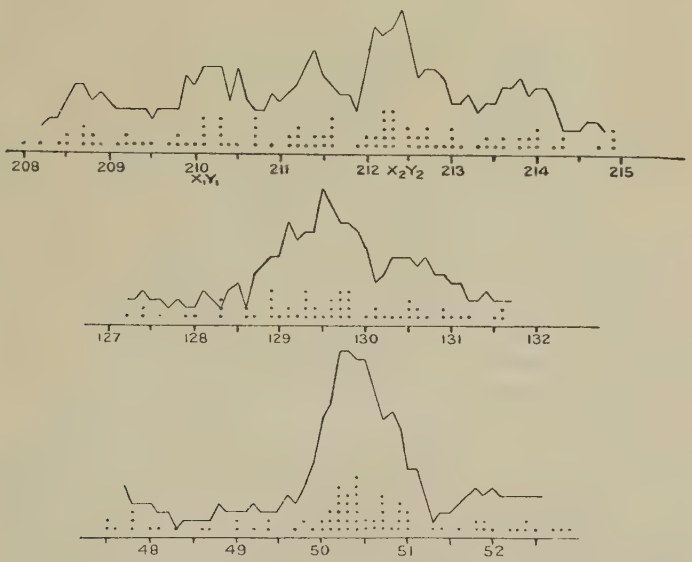
* For a few illustrations see my 'Analysis of Spectra,' pp. 153-6, 159-161.

† Phil. Mag. xxxix. p. 462 (1920).

‡ Astro. J. vi. p. 239 (1897).

of a kind which he says "I have never observed before." His 680 is of course the *u*-link, but the others still remain to be explained. A first step is to get some idea of their exact values and degree of variation. For this purpose their occurrency curves have been determined. They are given in the accompanying diagrams. In these each dot

Fig. 1.



represents an observed separation equal to the corresponding abscissa $\pm$·05, whilst the ordinates give the number of cases within $\pm$·2 of the abscissa value. A rather wide extent of variation was taken in the test as their actual values were unknown beforehand. The curves show at a glance that the X separation has a maximum occurrency about 212·3 with minor maxima about 210·2, 214, and possibly near 211·4, but the peak at 211 would largely disappear if the ordinates were taken =abs.$\pm$·01 instead of $\pm$·02. The L show a maximum near 129·5 and a minor one near 130·5, but the broad peak round 129·5 shows that there are a large number between 129·3 and 129·8. In sharp contrast to these the M shows a very great rise near 50·3 and no other, but again a considerable number within 50 to 51. The individual separations almost certainly have errors $<$·1, so that where they crowd together the majority should be regarded as real X, L, M, whilst of the sparse ones many may be merely numerical coincidences.

The linkages which emanate from the recognized series lines have been represented in maps, in which some latitude has been allowed in the new Rydberg separations. These maps are simply the raw material on which to base conclusions. It is not to be supposed that the lines are actually built up one after another in the way indicated in a map or are related to a system such as the ordinary series lines which depend on a regular sequence. Each line is an independent set of link modifications superposed on the two fundamental series terms of the map involved. There is even no *à priori* reason why we should expect identical line characters in differently linked lines, such as we might perhaps expect in similarly displaced lines. The map is a means of identifying them, and even if the inclusion of a particular line is inadmissible it may yet serve as a stepping-stone between for the discovery of others.

The details of each map are discussed in the notes to each. To save space a line is represented by a small circle with an included number referring to the accompanying list. The exact separations are entered in thick type. Where there are definite reasons for disallowing a separation as a true link, it is enclosed in [ ]. In order to guard against assertions that the observed separations are merely coincidences in a crowded spectrum, the separations of each line from the nearest observed line on each side are given in small figures, except where a — means that the next is a succeeding linked one. In a few cases excessive deviations from the values in the occurrency curves have been admitted where their reality has been suggested by neighbouring regularities.

The large number of exact separations of 680·11 or close to it is very noticeable in those maps which include lines of Hasbach's satelloid group, and which also are connected to the P (1) series lines. It is ·52 less than the normal u-link which suggests the $y = ·57$ displacement. The difference ·05 is equivalent to an observational error $d\lambda < ·005$, which is within our permissible limits, but the large number with the same value may raise some doubt. It will, however, be treated as a u-link with concurrent displacements.

If these maps be examined, paying regard to the separations from neighbouring lines, indicated by the attached small figures, it will be seen that the great majority are well isolated from others and consequently that the large number of examples of the new separations really represent some definitely related system, even although their values differ considerably from equality, especially in the L, M sets. This

reality is also emphasized by the numerous examples of the appearance of the L, M in similar collocations. The maps reproduce the well-known features of the e, u, v linkages, which need not now detain us. Details will be found in the notes appended to each map. It is, however, interesting to notice that in these Cu-linkages the u-links greatly predominate over the v. There are also a large number of examples of series inequalities, such as for example the first two links from $P_2(1)$ in map I. of $(-e-\cdot17)+(u+\cdot17)=-e+u+0$ ending in the satelloid of (2), or again $680\cdot11+681\cdot02=2(u-\cdot06)$. We pass on to the immediate problem, that of the nature and origin of the X, L, M separations.

5. In discussing the origin of these, three suppositions are at our disposal, in the light of present knowledge :—

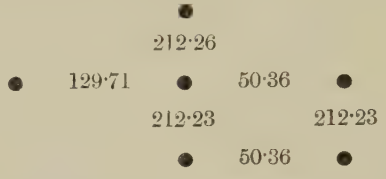
1. They are analogous to ordinary multiplet separations (different j-quanta), *i. e.* involve new "terms".
2. They are links formed in some way analogous to those already known.
3. They have their origin in displacements or successive displacements in one of the main terms entering into the lines involved.

If they are analogous to multiplet separations, these generally form an arithmetical progression. Landé's rule goes further and may be stated in the form that they should be proportional to a series of numbers differing by 2 and starting from some particular integer. In other words if s_1, s_2... denote the separations they form an A.P. with common difference s_2-s_1, and in Landé's rule the first number $=2s_1/(s_2-s_1)$. Now the separations in question do form an A.P. with common difference about 80. On Landé's rule the first number should be $100/80=1\cdot25$ and is not even an approximate integer. His rule would therefore exclude supposition 1, but his rule is only an approximate one. Nevertheless, consideration of Rydberg's "remarkable multiplet" shown with thickened connexions in map VI., 2, 3, 4—5, 6, 7—8, 9, 10, will show that they cannot all thus enter.

Moreover, from our present knowledge we infer that if they form a set of triplets, the sets must belong to the ionized ion. In that case they would not be associated with links dependent on the neutral atom, as in fact they are.

Again, the essential property of all known multiplets is that the separations appear as pairs which are never repeated as pairs in the same multiplet. In fact this is the experimental basis for the "principle of selection" in j. It

follows, therefore, that the 680·11 must be of a link nature quite independently of its close relation in value to the known u. The (5, 6, 7, 10) may then be put aside as merely sets parallelized by the u-link. The others with (11) added may be arranged thus:—



This indicates that if there is an analogy with doublets and triplets, the 212 must depend on one term and the other two 129, 50 on a second. So far as this particular set of lines is concerned, this may be the case for 129, 50, but it cannot be the case for 212. The various values for each 212 are extraordinarily close. We find two successive separations 212·26, 212·23 clearly really equal, and this cannot occur with successive displacements in the same term, for the same displacement must give a shift differing by more than ·03. This points to the supposition that the 212 are of the nature of links. It is easy to see also that 212 must be some link, and that 130, 50 cannot be displacements on one and the same unmodified term as in the ordinary series separations, since we find numerous cases of successions of separations near their values. If they are displacements in some term, they can only occur if that term is present. Now a search will show that 212 appears connected with known difference lines involving terms of all the known types. On the other hand, we do not find the 130, 50 connected with lines in which we can be certain that the term $p(1)$ does not occur and that they are numerous where it does. We will therefore consider the 212 sets and the 130, 50 separately.

The 212 *sets.*

6. Confine ourselves for the present to separations near 210·2, 212·3 quite definitely given by the occurrency curve. We get a few in the direct P linkage of map II. and some striking sets in the parallel chains of map III. A few occur in IV. (S 2), several in V. (D′ or inverse D), very numerously in VI. (probably P 1), many in VII. (probably composite) and in VIII. (portion ? to P). 210·68 is linked to Randall's X^*-p_12. My suggestions of $Q_1(1)$, $Q_2(1)$

* X is Randall's symbol x for what Shenstone calls d_21, and Y represents the latter's d_11.

have respective links of 208·7, 212·7. $Q_2(2)$, Shenstone's $s(1)-p_e$, has 209·50; 24643 or p_1-f3 has 208·47; 21282 ($? d_2 1-d_1 3$) has 212·58. Of Shenstone's combinations, $s(1)-p_d$ has 214·03, 212·10 in series, $Y-p_c$ has 212·63, 209·26 in series, $X-p_c$ has $u-210{\cdot}50$, $X-p_f$ has 211·11. It is attached also to some of the lines of Stücklen's multiplets and to many others not yet allocated. The above list contains lines depending on $s(m)$, $p(m)$, $d(m)$, $f(m)\,.\,d_2'1\,.\,Y$, and other terms. The separation then cannot arise from a term already present and must be of the nature of a link. That being accepted, the question arises as to its source. The $a \ldots d$, e links arise from $\pm\Delta$ displacements on $p_1 1$, $p_2 1$, the u, v from $\pm\Delta$ displacements on $s(1)$. It lies to hand, therefore, to test whether they arise from $\pm\Delta$ displacements in some other term. Naturally the first term to test is $d(1)$. The satellite separation of $d_1 1$, $d_2 1$ is very close to 27 and may be slightly larger, but the uncertainty will not appreciably affect the values. The values of $d_2(1)$ and $d_1(1)$, as well as their mantissæ, were given in R.A. in a paper † about six years ago. The values corrected to I.A. are

$$d_2(1) = 28415{\cdot}50 = N/(1{\cdot}964642)^2,$$
$$d_1(1) = 28388{\cdot}01 = N/(1{\cdot}965592)^2,$$
$$\text{with} \qquad \Delta = 7306{\cdot}9,$$

and we have to calculate the values of $d_2(1)(\pm\Delta)-d_2(1)$ and $d_1(1)(\pm\Delta)-d_1(1)$. Denote the values on d_1 by X and on d_2 by Y; X_1, Y_1 for the $+\Delta$ links and X_2, Y_2 for the $-\Delta$. *E.g.*,

$$X_1 = N/(1{\cdot}965592+7307)^2 - N/(1{\cdot}965592)^2.$$

The values calculated are

$$X_1 = 209{\cdot}88, \qquad Y_1 = 210{\cdot}21,$$
$$X_2 = 212{\cdot}27, \qquad Y_2 = 212{\cdot}54.$$

The agreement with our observed values is strikingly close. We have seen how in the occurrency curves the observed values crowd together round 212·3 and 210 with a very large number $= 212{\cdot}3 \pm {\cdot}2$. There can then, I think, be little doubt but that the 212 separations are links as calculated above. We thus discover a new fact in spectral laws of the greatest importance. Further support in favour of the X being links with the above values in Cu is afforded by

† Phil. Mag. xxxix. p. 463 (1920).

a study of the maps which show a large number of series and parallel irregularities, a phenomenon distinctive of true linkages. We find, for instance, amongst others,

Map II. $208{\cdot}54+211{\cdot}11 = 2X_1-{\cdot}03$

III. $211{\cdot}73+212{\cdot}69 = 2X_2-{\cdot}12$
$212{\cdot}18+680{\cdot}71 = X_2+u-{\cdot}01$

V. $213{\cdot}61+208{\cdot}86 = 2X_1-{\cdot}01$

VI. $1001{\cdot}23+210{\cdot}71 = e+X_2-{\cdot}13$

VII. $210{\cdot}56+214{\cdot}63 = 2Y_2+{\cdot}10$

7. If the law is general, indications of similar links should be expected in other elements, especially in Ag and Au of the same group. On account of its great importance in general theory, a preliminary test on the arc lines of Ag and Au has been made. The $d(1)$ data for silver * and gold † were given in former papers in this Magazine. They are reproduced here with the values of X, Y now calculated therefrom :—

	Ag.	Au.	
Δ	27789·1	113935	
δ	421·04	1406·7	
Sat. displ.	$23\,\delta_1$	$28\,\delta_1$	
d_2	$28997{\cdot}41 = N/(1{\cdot}944829)^2$;	$26735{\cdot}85 = N/(2{\cdot}025415)^2$	
d_1	$28925{\cdot}33 = N'(1{\cdot}947250)^2$;	$26477{\cdot}75 = N/(2{\cdot}035262)^2$	
X_1	808·22	2732·90	*·81* R.A.
X_2	843·61	3233·39	*·29* „
Y_1	811·24	2771·92	*·83* „
Y_2	846·76	3282·19	*·08* „

The arc spectra of these metals were then tested for separations of about these values, confining attention only to links from arc lines. No complete investigation has been made and only the arc lines as given by Kayser and Runge and by Kaspar were used, about 70 in Ag between 17638 and 44500 and about the same in Au. The linked lines now, however were sought for in their natural habitat of the spark spectrum. The result is given in the following lists, the values for Au being in R.A., an old hand-list in R.A. being at disposal. The observed separations are in thick type, and those of neighbouring spark lines are inserted in ( ), as in the maps.

* Phil. Mag. xxxviii. p. 316 (1919). † *Ibid.* xxxviii. p. 8 (1919).

Ag.

1.	(18, 15)	17932·14	812·57	18744·71	($-D'_{11}1$)			
2.	(30·18)	17913·90	843·57	18757·47				
	(15, 38)	46·89	810·58					
3.	(14, 86)	18342·73	849·18	19191·91	($D_{22}2$)			
4.				21943·15		808·75	22751·90	(271, —)
						855·25	98·40	(—, 14)
5.				24652·33[1]	($D_{22}3$)	850·68	25503·01[2]	(89, 10)
6.	(37,23)	25392·4	842·0	26234·48	($D_{11}4$)	851·64	27086·12	(29, 54)
7.				26941·61	(S_15)	857·7	27799·3	(126, 121)
8.				27584·4	($D_{11}5$)	853·	28437	(420, 18)
9.	(62, 181)	27209·38	851·14	28060·52				
10.	(29, 126)	27672·70	847·31	28520 01				
11.				28547·47		811·50	29358·97	(66, —)
						842·51	89·98	(–, —)
						853·90	29401·37	(—, 23)
12.				29551·79	(P_21)	811·60	30363·4	(5, —)
						842·14	93·93	(—, 11)
13.	(15, 61)	29231·58	810·47	30042·05				
14.				30241·03				
				846·95				
	(22, 20)	30279·75	808·23	31087·98		844·5	31932·5[3]	(116, 17)
				850·87				
				31938·85	(see 17)			
15.				30472·90	(P_11)	848·0	31320·9	(17, 40)
16.	(10, 11)	30679·3	851·8	31531·09				
	(8, 10)	30723·5	807·6					
17.	(36, 16)	31126·7	812·1	31938·85		810·57	32749·42	(128, 61)
	(12, 36)	31089 86	849·00					
18.	(15, 15)	31445·65	812·34	32257·99				
19.				36728·95		846·86	37575·90	(56, 39)
				848·76				
20.	(114, 23)	36767·4	810·3	37577·69				
21.				38818·93		804·2	39623·1	(38, 28)
22.	(23, 14)	40202·62	807·71	41010·33		807·75	41818·08	(43, 65)
23.	(18, 14)	40618·63	809·56	41428·19[4]		845·4	42273·6	(16, 12)→
24.	(16, 12)→	42273·6	811·8	43085·39		810·26	43895·65	(27, —)
						850·95	43936·34	(41, 22)
25.				43147·41		811·34	43958·75	(21, 27)
26.	(22, 11)	43005·71	842·67	43848·38[5]		812·65	44661·01	(40, 94)
27.				44458·68		806·57	45265·25	(55, 52)
28				44503·72		845·29	45349·01	(31, 17)

[1] Kaspar gives 24650·75. [2] By E.H. E.V. give ... 04·18.
[3] E.H. observe this and 31939·6.
[4] $809·56+854·4=X_1+Y_2$ a series inequality.
[5] $842·67+812·65=X_1+Y_2+·34$ „ „

Au.

1.				15791·60	**2777·81**	18569·41	(38, 8)
2.				15923·38 ($-D'_{22}1$)	**3290·34**	19213·62	(100, 207)
3.				17050·97	**2777·67**	19828·64	(90, 100)
4.				19113·51 ($-D'_{11}1$)	**2732·90**	21846·41	(8, 14)
5.	(30, 21)	18011·59	**2764·91**	20776·50 ($S_1 3$)			
6.	(11, 28)	17573·91	**3285·06**	20858·97 ($D_2 2$)	**3275·51**	24134·48	(60, 79)
7.	(17, 35)	18155·67	**3277·75**	21433·42	**3232·85**	24666·27	(50, 73)
8.	(125, 7)	18415·80	**3285·87**	21701·67	**3281·41**	24983·08	($6_{\frac{1}{2}}$29)
	(18, 12)	18467·56	**3234·11**	**2775·79**			
				24477·46 (see 14)			
9.				22273·24	**2772·15**	25045·39	(33, 10)
					3228·05	25501·29	(16, —)
					3235·85	09·09	(—, 19)
10.				22529·32 ($D_{11}3$)	**2770·87**	25308·19	(59, 29)
					3284·53	25813·85	(14, 9)
					3234·35	25763·77	(21, 19)
11.				22904·68	**2771·90**	25676·58	(14, 6)
					3225·93	26130·61	(18, 18)
					3290·06	26194·74	(27, 15)
12.	(75, 310)	20392·38	**2774·49**	23166·87	**2735·84**	25902·71	(28, 20)
					2766·61	25933·48	(6, —)
					2774·61	41·48	(—, 42)
					3229·36	26396·23	(61, 28)
					3279·90	26446·77	(22, 34)
13.				23567·34	**2767·78**	26335·12	(23, 61)
					3228·23	26795·57	(13, 47)
					3274·69	26842·03	(47, 46)
14.				24477·46	**2724·98**	27202·44	(11, 8)
					33·20	10·66	
					3234·12	27711·58	(6, 20)
					3281·19	27758·65	(27, 25)
15.	(21, 27)	21365·24	**3226·83**	24592·07 ($S_2 3$)	**2737·27**	27329·34	(28, 5)
	(9, 20)	21818·29	**2773·78**		**2770·11**	27362·18	(5, 20)
	(14, 11)	21860·79	**2731·28**		**3281·26**	27873·33	(40, 40)
16.	(45, —)	21973·73	**2765·33**	24739·06	**2775·65**	27514·71	(13, 5)
	(—, —)	22001·67	**2737·39**		**3233·44**	27972·50	(17, 62)
	(—, 89)	22013·58	**25·48**				
17.				25571·39	**3235·01**	28806·40	(11, 152)
18.	(23, 221)	22874·60	**2772·21**	25646·81			
19.	(9, 21)	25396·77	**2734·92**	28131·69			
				3287·18			
				31418·87			
20.	(12, 7)	26105·71	**2728·01**	28833·72	**3237·19**	32070·91	(25, 109)
21.	(20, 13)	27382·63	**2726·51**	30109·14	**3236·20**	33345·34 ? Pt	(42, 32)
	(5, 21)	27334·57	**2774·57**				

Au (*continued*).

22.		.....	**3282·98**	30617·55			
	(20, 13)	27382·63	**3234·92**				
23.	(2, 39)	27444·78	**2772·63**	30217·41			
	(39, 18)	27483·17	**2734·24**	**2739·76**			
				32957·17			
24.	(7, 52)	28174·96	**2769·07**	30944·03			
	(46, 24)	27661·13	**3282·90**				
	(6, 20)	27711·58	**3232·45**				
25.	(40, 41)	27913·86	**8280·48**	31194·34			
26.	(22, 66)	28689·63	**2729·24**	31418·87			
27.		.....	**3280·58**	31970·13	**3280·24**	35250·37	(27, —)
					86·21	56·34	(—, 22)
28.				32904·37	**2769·66**	35674·03	(—, 85)
					2730·37	35634·74	(185, —)
29.				33001·33	**2775·19**	35776·52	(17, 172)
30.				33052·05	**3286·48**	36338·53	(390, 29)
31.				33165·51	**3276·71**	36442·22	(34, 136)
32.	(79, —)	30823·67	**2771·82**	33595·59	**2772·11**	36367·70	(29, 7)
	(—, 16)	28·51	**67·08**				
33.	(26, 38)	30498 87	**3230·89**	33729·76			
				3282·46			
				37012·22			
34.	(47, 11)	31017·94	**2731·98**	33749·92	**3276·15**	37026·07	(35, —)
	(54, 26)	30472·47	**3277·45**		**84·65**	34·57	(—, 22)
					3229·18	36979·10	(35, 12)
35.	(11, 23)	31028·43	**3283·24**	34311·67	**3278·08**	37589·75	(81, 118)
36.	(83, 103)	31669·32	**2732·64**	34401·96			
37.	(20, 26)	31941·23	**2728·26**	34669·49	**3278·72**	37948·21	(15, 39)
38.	(146, 16)	33147·81	**3227·06**	36374·87	**3230·21**	39659·88	(33, 56)
39.	(77, 46)	33729·55	**3282·67**	37012·22	**2735·16**	39747·38	(32, 54)
40.				37179·69	**3231·37**	40411·06	(39, 94)
41.	(28, 134)	34120·84	**3236·78**	37357·62 ($P_2$1)	**2765·64**	40123·26	(19, 17)
42.	(17, 76)	34567·63	**3277·08**	37844·71	**3233·34**	41078·65	(14, 6)
43.				38595·88	**2770·88**	41366·76	(12, 40)
44.				39291·95 F_1(2)	**2776·83**	42068·78	(15, 76)
					3281·17	42573·12	(62, 20)
45.	(12, 137)	36590·77	**3229·23**	39820·00	**2773·07**	42593·07	(20, 51)
46.				41172·94 ($P_1$1)	**3282·76**	44456·70	(8, 39)
47.	(86, 84)	39542·25	**2733·89**	42276·14	**2767·29**	45043·43	E.V. (25, 72)
					9·74	45·86	E.H.
48.	(56, 32)	39715·01	**2775·79**	42490·80	**2731·06**	45221·86	(52, 7)
					3279·56	45770·36	(33, 250)
49.	(41, 16)	41048·04	**2772·74**	43780·72			
	(78, 41)	41007·98	**2732·68**				

Very many of these lines occur in high wave numbers, and for these observation errors may amount to a unit or more in the wave number. In several cases different observers vary so much as to suggest different lines (? displaced). In Ag there seems to be a distinct clustering round 850·91 with four readings differing from this by $-\cdot23$, $+\cdot23$, $-\cdot04$, $+042$, pointing to a displacement in the case of a Y_2 link. Near the calculated values we find

for $Y_1=811\cdot24$ values 810·58, 11·50, 11·60, 10·47, 10·57, 10·3, 11·8,

$X_1=808\cdot22$ „ 808·75, 8·23, 7·65, 7·75, 7·71,

$Y_2=846\cdot76$ „ 847·31, 6·95, 6·86,

$X_2=843\cdot61$ „ 843·57, 2·0, 2·67,

within their respective observational errors. So also in Au near $Y_1=2771\cdot83$ are 2772·15, 1·90, 2·21, 2·63, 1·82, 2·11, 2·74,

$X_1=2732\cdot81$ „ 2732·90, 2·85, 3·20, 3·44, 2·46, 1·98, 2·64, 3·34, 3·89, 2·68,

$Y_2=3282\cdot08$ „ 3281·41, 1·19, 1·26, 2·98, 2·90, 2·46, 2·67, 2·76, 1·17,

$Y_1=3233\cdot29$ „ 3232·85, 4·11, 2·85, 4·12, 3·44, 4·24, 3·34.

Even if some of the separations adduced have no relation to X, Y links, the evidence from the mass of cases is in striking support of their existence. For instance, of the 62 arc lines in Au 48 show these attached links, many of them several. We have to remember that with links in general we get also simultaneous displacements in one of the two terms of the series lines with which they are associated. When we know these terms we can calculate the oun shifts and we are generally enabled definitely to settle the actual displacements. When these shifts are large, as for instance in Au or for first order terms in elements with smaller ouns, an allocation is often convincing. We can of course only apply this principle when the series line to which a chain belongs is known. In the above data in Au for example, we have cases belonging to $S_1(3)$, $S_2(3)$, $D_2(2)$, $D_{11}(3)$, $D_1'(1)$, $D_2'(1)$, $P_2(1)$, $P_1(1)$. Now in gold the oun shifts in the terms involved are:

$s1.$	$p_1 1.$	$p_2 1.$	$d_1'1.$	$d_2'1.$	$s3.$	$d2.$	$d3.$
39·9	10·77	13·90	22·74	23·18	1·723	2·914	1·228

The large shifts involved in $s\,1$, $p\,1$, $d\,1$ are so great that the links would be distorted beyond the deviations we have allowed for in forming the above lists. The material at hand for the above series lines treated on this basis gives the following results. The displacements are supposed to have been produced in the spark lines.

$D_2'1$	one	$(\delta_1)D(\delta_1)$	gives	9·28	makes sep.	$+3281{\cdot}08=Y_2-1$	$d\lambda=$ ·26 *
$D_1'1$	one	0				$+3732{\cdot}90=X_1+{\cdot}09$	$-{\cdot}02$
$S_1 3$	one	$-\delta$ on $s\,3$	„	$-6{\cdot}89$	„ „	$-2771{\cdot}80=Y_1-{\cdot}03$	·004
$S_2 3$	six	$-\delta$	„ „	$-6{\cdot}89$	„ „	$-3233{\cdot}72=X_2-{\cdot}43$	$-{\cdot}09$
	back	δ_1	„ „	1·72	„ „	$-2772{\cdot}06=Y_1+{\cdot}23$	$-{\cdot}05$
		$-\delta_1$	„ „	$-1{\cdot}72$	„ „	$-2733{\cdot}00=X_1+{\cdot}19$	$-{\cdot}04$
		$3\delta_1$	„ „	5·17	„ „	$+2732{\cdot}10=X_1-{\cdot}71$	* (·10)
	forward	$-\delta_1$	„ „	$-1{\cdot}72$	„ „	$+2771{\cdot}83=Y_1+0$	0
		0				$81{\cdot}26=Y_2-{\cdot}82$	* (·10)
$D_{22}2$	two	δ_1	„ d_2	2·914	„ „	$-3282{\cdot}15=Y_2+{\cdot}07$	$-{\cdot}02$
		$-2\delta_1$	„ „	$-5{\cdot}83$	„ „	$3281{\cdot}34=Y_2-{\cdot}74$	* (·12)
$D_{11}3$	three	$-\delta_1$	„ d_3	$-1{\cdot}23$	„ „	$+2772{\cdot}10=Y_1+{\cdot}27$	$-{\cdot}04$
		$2\delta_1$	„ „	2·45	„ „	$+3282{\cdot}08=Y_2+0$	0
		δ_1	„ „	1·23	„ „	$+3233{\cdot}22=X_2-{\cdot}07$	·01
$P_2 1$	two	0				$-3236{\cdot}78=X_2+3{\cdot}49$	† $-{\cdot}4$
		0				$+2765{\cdot}64=Y_1-6{\cdot}19$	† $+{\cdot}4$
$P_1 1$	one	0				$+3282{\cdot}76=Y_2-{\cdot}68$	$-{\cdot}03$

With the exception of those marked with * † all the new values are within observation errors, and the agreement is convincing as they occur with such large oun shifts and with displacements on a single term (the first excepted). The lines marked * may be false links or, since their deviations are the same (·8), this may be due to some double displacement, *e. g.* (1) $S_2 3$ (7) gives $-{\cdot}84$ and (1) $D_2 2$ (5) gives ·67. The † suggest also the entrance of double displacements, *e. g.* (2) $P_2 1$ (6) shifts 3·6.

We shall now in discussing the maps consider the existence of Δ links based on the d (1) terms as established and that Rydberg's 212 separations comprise the links in question. The extraordinary importance of this fundamental quantity Δ in the constitution of spectra is thus further emphasized.

8. We are now in a position to discuss the satelloid data for link modification, taking the various maps in succession.

Map I. (2, 5, 8, 6) involving ($7x$, $10y$, $12x$, $9x$) * of Table I. The satelloid of (2) occupies the exact $u-e$ from P_1 and a Rydberg's u is continued on from it. Then a new chain starts from the main line to (4) and passes to the first satelloid of (5) on to that of (8) and continues to (10). Again new chains start from the main lines of (5, 8) and other modified ones start from the satelloids of (6). That from the red satelloid of (6) and the $+u$ to (13) form a parallel inequality since $1000{\cdot}06-681{\cdot}02=e-u+{\cdot}13$.

Map II. This is an extension of I involving the X, L, M separations. It contains three additional satelloids (3, 17, 30) or ($8y$, $11x$, $15x$) of Table I. Note the series inequalities from each satelloid of (3), viz. $682{\cdot}00+679{\cdot}36=2u+{\cdot}10$ and $693{\cdot}05+691{\cdot}41=2v+{\cdot}30$. When three lines show a series inequality it means that the extreme lines suffer the same displacement, so that here the satelloids represent the normal positions. A normal L separation links the second violet of (5 I) to the extreme red of (17), whilst a true u passes from the main of (17). From the satelloid of (8 I) is a series inequality $208{\cdot}54+211{\cdot}11=2X_1-{\cdot}03$. (30) is an x satelloid—sep. $5x$—and the modified e links suggest an unobserved satelloid at $-y$ of the one seen, making exact e.

Map III. contains sets parallel to those of (8, 10) of I, and is noticeable for the number of X links. (3, 4, 5, 10, $13a$) are the satelloids ($16y$, $13y$, $14x$, $18y$, $17x$) of Table I. Note the true u to the extreme satelloid of (3). Indeed, if (1) is ·08 ($d\lambda={\cdot}008$) too large, the two successive links become exact, viz. $X_2=212{\cdot}26$ and $u=680{\cdot}63$. Also, while we get X_1 between the mains of (4, 5) we also find it between two of their satelloids. In (4) the modified u requires an unobserved satelloid at $-2y$ (the violet is $5y$). In (5) the first satelloid gives a normal M forward, the second has X_1 back and a modified v which indicates a third satelloid displaced a further x. So in (10) the links are definitely attached to the satelloids, but are modified indicating unobserved ones, as the u, e form a series inequality since $679{\cdot}95+1000{\cdot}62=u+e+{\cdot}16$; whilst the $209{\cdot}26$ becomes an exact X_1 if there be an additional violet, y further out. In ($13a$) we get a remarkable example of the satelloid representing the true linked line with the formula $P_1(b+1)\,.\,3u\,.\,v+0$.

Map VI. In the P(1) portion (16, 47, 51) are ($5y$, $6y$, $4y$) of Table I. In (16) the links e, L. belong definitely to the first violet satelloid. At (47), again, the composite link $u+v$ goes to the first violet satelloid. In (51) the main only is involved.

* The x, y refer to the x, y nature of the sets in Table I.

Map VIII. In this occur (5, 7) or ($1y$, $2y$) of Table I. The map was drawn from S (3), but these sets are excluded by false links. (5) shows no links, but (7) is noticeable for a pair of parallel links from its extreme satelloids. It will be recognized that the statement at the end of § 3 is fully justified.

The 130, 50 *separations.*

9. Returning now to the consideration of the L, M separations, a glance at the maps will show that they occur in those depending on P(1), S, D, D_1' links, of which the only common term is $p(1)$. On the contrary, they do not appear connected with the following, which do not contain the $p(1)$ term. The data are in wave number.

P(2) or region.			
36172 104	$d_2'-p(2)$	21503 532 F(3)	All Shenstone's sets except his p_c, p_d
20646 543 574	$d'-d(1)$	23929 $F_1(4)$	$d_2'-p_e$
		25328 F(5)	$Y-p_h$
		27338 584 Q_1	$d_2'-p_h$
21494 298	$d_2 1-d(3)$		
		45821 Q_2	

Of Stücklen's two multiplets (18 lines in all) numerous X links are found attached but only one M to a very doubtful constituent of her second multiplet, the same as the Q_2 above. The origins of Shenstone's sets are not yet known, and some of them appear to be link related. His $Y-p_c$ is (13) of map III., his $d_2'-p_c$ is a satelloid, (11) of Table I. and (17) of map II. Also his p_d term is possibly merely a link connexion to p_c. His $d_2'-p_d$ is (23) of map I. All these maps belong to P(1) connexions. $d_2'-p_e$ is (16) of III., *i. e.* belongs to P(1). $Y-p_h$, $d_2'-p_h$ come in IX. and are there treated as involving $p(2)$. Also, $p_g-p_h=2e+Y_1$ and $d_2'-p_g$ is a satelloid and (3) in III. Thus the Shenstone exceptions are probably only apparent except in IX., where the two L, M may be spurious.

If, then, the L, M separations depend on displacements in some one term, that term must be the $p(1)$. We find several successions of L separations. If it is possible to transform each to some common value by displacement on the terms known to be involved in each case, it is an argument in

favour of a link theory. If, on the contrary, they constantly increase or constantly decrease, we are led to suspect successive displacement as the origin. There is one such long series in map II. with 130·02, 128·91, 130·27, 128·88, 129·81; but we shall see reason to regard the 130·02, 128·91 as mere coincidences. There is another of 132·96, 132·23, 128·93, 130·98 in map IV. which show a tendency to regular decrease, especially when the 128·93 is seen to follow an enlarged u, i. e. a u-link which has encroached on it by 3·30. Very frequently the L, M occur in connexion. Also successive M's are frequently met with. In map VI. this is very noticeable. Here not only is the Rydberg set repeated by the u-link but we get similar repetitions by the e, and we find the increasing values 129·71, 130·10, 52·04, 53·79. Another increasing set is in map V. of 47·50, 50·43, 51·84. All these examples point to shifts by successive displacements of about the same amount. We shall test the data on this basis.

To produce shifts of about these amounts the displacements must be near $a=26\delta=104$ ouns and $b=10\delta=40$ ouns. These produce the following shifts :—

$+a$ on p_1	$=128{\cdot}05$	on p_2 $=129{\cdot}56$
$-a$ „	$=128{\cdot}84$	„ $=130{\cdot}39$
$+b$ „	$=49{\cdot}31$	„ $=49{\cdot}89$
$-b$ „	$=49{\cdot}47$	„ $=50{\cdot}05$

Provisionally we shall use these a, b as near the normal displacements. The testing is rather tedious as each case has to be specially calculated. The procedure is, however, rendered easier by first calculating the values of the displaced p_1, p_2 for successive b and a together with the shifts per oun for each value. For instance, if say, $(-3a+b-1)p_1$ is required, $-3a+b-1=-68\frac{1}{4}\delta=-7b+7$. The value required is given by the table for $-7b$ and the change per oun. Thus the new value of the p_1 is $31873{\cdot}21-7\times1{\cdot}2554=31864{\cdot}42$. The table is given as an Appendix. Since $\Delta=50\delta$, $(-xb)\,p_1=(5b-xb)p_2$. Also it should be remembered that the shift in a term is in the opposite direction to the displacement, so that for instance a positive displacement entered on the left of the series line symbol diminishes the wave number, whilst if on the right it increases it. Thus $P_1 1(-)$ is a diminished wave-number whilst $(-)S_1 m$ is increased, although the displacement on p_1 is the same in both. It will be sufficient here to discuss in some detail a few important illustrative cases only. A more complete discussion is given in the notes to the maps, although,

as the general laws of link connexion are now well established, all the lines of all the maps are not dealt with.

We begin with a portion of map IV., containing lines based on the $S_1(2)$, $S_2(2)$ series lines. The majority of the wave-lengths have been carefully measured by one observer, who has given estimates of his probable errors (·01 to ·05 Å.U.); also with the small wave numbers involved the ratio $dn/d\lambda$ is small. Further, the map itself is a reliable one for the ordinary known links. The Cu spectrum is noticeable for the large number of separations close to that of the series doublet (248·44). A few have been included in this map, although there are others. The lines in the region measured by Meggers are well spread out, but there are a few regions of smaller wave-length, where the lines come close together, and in many cases are seen to depend on displacements of a few ouns. Some of these are indicated in the map by one or two additional circles. In all cases the usual displacements concurrent with links depend on a few ouns only, so that the shift per oun on $s2$ may be taken as constant, those on the p will of course vary largely and are given in the Table A in the Appendix. Its value for $s2$ is ·5856. The linkage in general is supported by the large number of similar and parallel links. It is noticeable also for the back L-separation and for the long double links $e+u$ from both S_1 and S_2 without representatives for e or u alone. That from S_1 is in defect by 1·89 accounted for by $(+\delta_1)S_1(-\delta_1)$, which shifts $1·235+·585=1·82$ with $dn=·07$ (prob. O, E = ·1). The other from S_2 is ·48 in defect accounted for by $(-\delta_1)S_2(-3\delta_1)$. We shall consider specially here for our immediate purpose of discussion of the origin of the L, M, the long chain from S_2 round by (2, 3, ... to 10). First we notice the corresponding 130·23 back from S_1 and 132·96 from S_2. Now, $(a+2*)S_1$ produces a shift 130·50, i. e. $dn=·27$ and is too large. But $(a-2)S_1(-8)$ has $dn=·05$. Similarly the back link from S_2 is met by the same $a-2$ and is $(a-2)S_2(-10)+·03$. In the S_1 the long linked line to (4) is $(1)S_1(-1).e.u+·07$, and the corresponding one from S_2 is $(-1)S_2(-3).e.u+0$. The S_2 chain we are to consider has the constitution — starting from (1)—$L+(e+u)+L+u+L+u$ and then returns by $-M-u-u+L$ to (11). We note also the corresponding successive L, M at (5) and at (7).

* Here and in the sequel in denoting displacements we shall omit δ_1, and a number will denote number of ouns.

(3) is 132·23 ahead of 2, produced exactly by $(-a-1)\,|\,(1)$, so that the line is $(-a-2)\,S_2(-2)\,e\,.\,u+0$.

(4) is $u+3{\cdot}30$ ahead, i. e. u with concomitant displacement $(-4)\,|\,(-3)+{\cdot}03$, the line is therefore $(-a-6)\,S_2(-5)\,.\,e\,.\,2u+{\cdot}03$.

(5) is 128·94 ahead. This is L modified by the foregoing displacement. The formula is $(-2a)\,S_2(4)\,e\,.\,2u+{\cdot}06$, or the L appears as a normal additional on $(-a)\,S_2(4)$.

(6) is $u-1{\cdot}29$ ahead and is $(-2a+1)\,S_2(4)\,e\,.\,3u+{\cdot}03$, the oun displacement giving 1·265.

(7) is 130·98 ahead and is $(-3a-1)\,S_2(-2)\,e\,.\,3u+{\cdot}01$.

(8) is 50·21 (*i. e.* M) behind. It is $(-3a+b-2)\,S_2(-3)\,.\,e\,.\,3u+0$, the M being produced by $(b-1)\,|\,(-1)$.

(9) is $u-{\cdot}02$ behind and is $(-3a+b-2)\,S_2(-3)\,.\,e\,.\,2u+{\cdot}02$.

(10) is $u+{\cdot}13$ behind and is $(-3a+b-1)\,S_2(-1)\,e\,.\,u+0$.

(11) is 129·10 ahead and is $(-4a+b-2)\,S_2(-9)\,.\,e\,.\,u+{\cdot}01$.

(16) is 51·64 ahead of (7) and is $(-3a-b-2)\,S_2(-2)\,e\,.\,3u+{\cdot}01$.

We have now a cycle round from (3) to (10), separated by 211·61. If this represents some modified X-link, then one of the L or M in the chain must be false. If it is not, then (3), (10) are simply mutually displaced, viz. comparing their formulæ above by $(-2a+b+1)\,|\,(1)$. This, as we have seen, gives exact 211·61. Again, the L sep. 129·10 to (11) must have a different signification according to the two suppositions, viz. displacement on $(-a)\,S_2$ if 211 is a link, and on $(-3a+6)\,S_2$ if it is merely a displacement and the chain is real. We should therefore be able to use these two facts to get a decision.

A. If 211·61 is a link it is one of $X_1+1{\cdot}73$, $X_2-{\cdot}66$, $Y_1+1{\cdot}40$, $Y_2-{\cdot}93$. The displacement per oun on $(-a)\,p_2$ is 1·257, and I see no simple arrangement to meet the deviations except $(1)\,|\,(1)=1{\cdot}257-{\cdot}585={\cdot}67$, which is good in itself for $X_2-{\cdot}66$, but with so many choices we might expect at least one coincidence. Again, on this supposition 129·11 depends on $(-a)$ on $(-a)\,p_2$ giving 131·18 with 1·265 per oun on the p_2. The 129·11 is therefore $(-2a)\,p_2-(-a)\,p_2-2{\cdot}07$. I can see no way to get near the 2·07 by multiples of p and s shifts. This therefore speaks strongly against the X-link supposition for 211.

B. Here, as we have seen, the shift 211·61 is exactly given

by the displacement theory, and at the same time 129 falls in naturally as an L separation with error $dn = \cdot 01$ or $d\lambda = \cdot 005$. We thus get striking support for the reality of the chain here discussed and the suggested origin of the L.

We have here a remarkable regularity in alternation of link and displacement. To show this we reproduce the values found above, starting from (1) which is really $(a-2)S_2$:

$$(a-2)\,|\,(-10)\text{——link——}(-a-2)\,|\,(-2)\text{——link——}$$
$$(-2a)\,|\,(4)\text{——link——}(-3a-1)\,|\,(-2)\text{——}.$$

A similar system of alternating links and displacements exists in the Au $S_1(3)$ * linkage, the links involved being the $a = 3195$ † and the successive displacements by Δ, Δ being the large number 113961. As in the present case this also starts by a backward displacement Δ, and the chain runs from $+\Delta$ to -3Δ. If X denote the line 23966 in $\text{Au} = S_1(3) + a(2)$, we may write the set:

$$(\Delta)X,\quad X,\quad X-a(2),\quad (-\Delta)X-a(2),\quad (-\Delta)X-2a,$$
$$(-2\Delta)X-2a,\quad (-2\Delta)X-2a-a(4),\quad (-3\Delta)X-3a,$$
$$(-3\Delta)X-4a(1).$$

i. e., alternate displacements by $-\Delta$ and alternate link deductions $= a$. The parallelism is very striking. The values of the lines discussed above may be tested by direct calculation ‡.

* Trans. Roy. Soc. 217. p. 382 (1916).

† The a link, not the $a = 26\delta$ of the present paper.

‡ *E. g.* take $(10) = (-3a+b-1)S_2(-1)\,e.u.$ Here $-3a+b-1 = -68\delta-\delta_1 = -7b+7\delta_1$. The table in the Appendix shows that $-7b$ increases the limit by 352·82 and the oun shift is 1·270. Hence

$-7b$	increases	*352·82*
$+7\delta_1$	decreases	*8·89* $= 7\times 1\cdot 270$
		343·93
$-\delta_1$ on s	decreases	*·58*
		343·35
	$S_2(2) =$	*12601·80*
	$e =$	*999·80*
	$u =$	*680·63*
		14625·58

which is exactly the value observed.

Taking the L, M displacements as following one another in the chain, they are successively $-a+2$, $-a-2$, $-a+2$, $-a-1$, $b-1$, $-b$, $-a$. If the L, M depend on definite, the same displacements, with small concomitant ones, the values indicated by this map are a, b. In fact the deviations shown come in by the necessity of making the formulæ fit within O.E. If slightly larger O.E. be admitted the formulæ in question may be written, dropping the link signs:

$$(a)S_2(-6)+\cdot15\ ;\ S_2\ ;\ (-a)S(2)+\cdot12\ ;\ (-2a)S(4)+\cdot06\ ;$$
$$(-3a)S+\cdot11\ ;\ (-3a+b)S(1)+\cdot20\ ;\ (-3a-b)S(2)+\cdot21\ ;$$
$$(-4a)S(-5)+\cdot21.$$

The 5th, 6th, 7th depend on Aretz and may be allowed, but Meggers definitely excludes the 1st, 3rd, and last.

We take our next illustration from map VI. This map is remarkable for the number of exactly equal separations and of parallel repetitions of sets produced by e, u, and X links —the v here playing a very subordinate part. It was first drawn as starting from $S_1(5)$, with which it is connected through the large 214·86 link, only introduced because in arranging the raw material wide limits were admitted in searching for the X separation, with at that time uncertain values. Also $D_{11}(4)$, a very weak and unstable line only observed by Hasbach, is 208·32 from (12), or the more accurate $D_{12}=D_{22}-\nu$ distant 210·64. Neither of these separations is near the calculated values nor the maxima of the occurrency curves, and it would appear *à priori* extremely unlikely that such a definite and well-marked linkage should be associated with these weak lines. But the lines at (24) (25) appear in the P(1) map, thus indicating association with the P(1) lines. Moreover, the map contains some of the satelloid lines, and as the connexion of P(1) with other satelloids is quite definite this is an additional indication that the map is based on the P system. The line at (24) is (12) in map I. with the value $2e\,.\,u\,.\,P_1(-1)\,.\,v-3y+0$. No. (1) of the present map lies on a complete cycle through (24) and thus has two chains to it, viz. (L, M, X now representing link types),

$$-L+X+e+L^* \qquad = e+X,$$
$$-X+M+e-M+X+X = e+X.$$

* A series inequality, since $1000\cdot95+127\cdot36=e+128\cdot51$ with a normal L and the 1·15 on e is $2y+\cdot01$.

Hence (1) is (24) $-(e + X)$ links +small displacements, and *does not involve* the L, M separations themselves. Thus the link connexion of (1) is (taking X_2) $= X_2 . 3e . u . P_1 . v = 27583{\cdot}38$ by calculation, while (1) itself is 27584·18 or $X_2 . 3e . u . P_1 . v + {\cdot}80 = Y_2 . 3e . u . P_1 . v + 1{\cdot}07 = Y_2 . 3e . u . P_1 . v + 2y - {\cdot}07$ or $2x - {\cdot}01$. The important point is that (1) depends on $P_1(1)$ with a possible one or two ouns displacement. For our purpose of testing the displacement theory as the origin of the L, M separations the attached links do not affect the discussion. We may write (1) as $X_2 . P_1 + Z$ where Z is a number, and the L, M values will depend only on P_1. In other words, if we discuss the various lines connected with (1) treated as $X_2 . P_1$, their real values are those thus deduced +Z. To indicate this we shall write Q for $P_1 + Z$, so that the actual line at (I) is $X_2 . Q$. Starting from (1) there are the set (1, 2, 3, 4, and 49) with the separations 132·22, 50·36, 129·71, and 42·23, the last only introduced because of its $-u$, $+X_2$ links, parallel to those of the others. The formulæ (see notes to map) show that the first set depend on $-a$, $-b$, $-a$ displacements in p, with concomitants in other terms. The 42·23 of (49) may be M greatly distorted by other displacements. The arrangement shown in the tables makes its p-displacement $= -b - 2$, but it has no weight for the present discussion. With these four lines we get a set of four linked by $-u + y$, and another set by $+X_2$, involving the same a, b, a, b displacements but of course not serving as additional evidence. We get, however, an independent set of four linked to (3) by $-X_2$ with separations 130·10, 52·04, 53·79. Again, the formulæ show that they depend on successive p displacements of a, b, b. From these and (3, 8) we get corresponding lines linked by e. There is another L, M set in this map between (26, 27, 28) of 128·93, 50·40 again produced by a, b. Lastly, there are parallel isolated sets 124·91 and 133·07 from (31, 32). If R stands for $3e . X_2 P_1(-a - b - 2) . 2u . v - 3y + {\cdot}10$, (34) is R + 125·01 and (33) is $Y_2 . R + 133{\cdot}21$. Now $+a$ on R shifts 129·15, so that these lines are $R(a) - 4{\cdot}14$ and $Y_2 . R(a) + 4{\cdot}06$. These are within O.E. ($dn = \pm {\cdot}1$) of being equally and oppositely displaced in some independent way met by $7y$—in other words, they are L lines dependent on a. This map therefore affords strong support for the present theory. The argument is strong because the lines are very accurately measured and the oun shifts at disposal are large, 3·43, and 1·24, but it is weakened in some instances by the small but definite displacement unit, $y = {\cdot}57$.

Still dealing with P relations we may take map II., which comprises X, L, M separations dependent on the lines of map I. The notes to this map are well worth studying for the ordinary link effects. Here we confine attention to the L, M separations. Referring to the map and notes, we see at once that several false L, M are present. Thus, 130·02, 51·90 from P_1, P_2 to linked lines are excluded. For the same reason, of the two from (13), 128·91+130·27, at least one must be a false L and there must at least be one false in the cycle (17, 18, 19, 8I to 5I). The 53·15 of (2) from P_2 looks excessive, but so also does the succeeding 130·94+3·58=134·52 to (3). The two together, however, form a more normal L—M and give the formula $P_2(-a+b-1)+\cdot03$ for (3), whilst (2) becomes $P_2(b+2)-3y-\cdot01$. Again, the 50·04 to (8) is produced by a displacement of b alone. (10) is displaced an exact 3 ouns from (9), and the 50·04 is again given by b. All this set strongly support the a, b displacement theory. The separation of 50·30 from 4I *may* be false, although the formula is within O.E. and gives $-b$. The formula for (13) requires $-a$ and clearly shows that of the two L on either side it is 128·91 which must be excluded, whilst the two 128·88 and 129·81 fall in with great exactness but require $a-1$ and $a+2$. Again, (17, 18) fall in very closely on the supposition that 129·54 is real, and the defective formulæ for 129·80 based on this and for 50·25 based on 8I support the former by excluding these. There are a whole set from (21).

The formula for (21) is $X_1 . e . (-2)P_1(a+b) . 2u . v-y-\cdot06$. On this

$-(a+4)$ gives $-132\cdot94$, *i. e.* the observed separation to (29).

$-b$ gives $-49\cdot15$ and (22) becomes

$X_1 . e . (-2)P_1(a-b+6) . 2u . v+\cdot24$ within O.E. of this line.

(23) is ... $-50\cdot60$ and $-(b+1)$ on $a-b+6$ gives $50\cdot51$

$$= X_1 . e . (-2)P_1(a-2b+5) . 2u . v-\cdot09.$$

(24) is ... $-130\cdot55$, $-(a+1)$ on $a-2b+5$ gives $-129\cdot80$ and the formula may be written

$$X_1 . e . (-2)P_1(-2b+4) . 2u . v+y-\cdot08.$$

The displacements for 132, 48, and 50 fall in quite naturally, but the last is artificial and the 130 may not be a real L.

Lastly, map V., depending on the inverse D set, contains a large amount of material dealing with the X, L, M separations. The oun displacements are large—2·39 for d' and

1·23 for p_1, so that conclusions as to displaced lines may be trusted. On the other hand, a large number are spark lines and the possible O.E. are larger than in some of the other maps. The map, as drawn from the observed material, shows very many false cycles indicating that there must be a number of spurious links present. The discussion of the displacements (see notes to map) definitely excludes many apparent links, and in the end it is found that all the false cycles have disappeared with the exception of the two *e*, *u* links to (10), either of which are met by possible displacements though one at least must be spurious. The 998·66 is repeated again between (13, 18), so that the 690·48 may be the spurious. The reader should follow carefully through the notes to this map.

The foregoing discussion is sufficient to show that if the M, L depend on displacements on the *p* term those displacements are respectively $b = 10\delta$ and $a = 26\delta$. The displacement for the doublet separation 248·44 is 50δ. These numbers are respectively 3^2+1, 5^2+1, 7^2+1. When we remember that the corresponding values for the doublets in Ag and Au are * 8^2+2 and 9^2 we cannot but realize that some essential relation is here indicated.

Summary.

The paper has for its main object the determination of the origins and nature of the separations in the copper spectrum in the neighbourhood of 680, 212, 130, 50, pointed out by Rydberg many years ago. The 680 is the ordinary *u*-link, but the other three extremely well-marked occurrences have hitherto remained unrelated. The result is to show :

(1) That the 212 are links formed by Δ on the $d(1)$ term in the same way as those already recognized are formed on the *p* and *s* terms, thus further accentuating the great part which the quantity Δ takes in the general constitution of spectra.

(2) The 50, 130 seem to be of a quite different nature and to be due to successive displacements of 10δ, 26δ in *p* terms, that producing the doublet separation of 248·44 being 50δ.

(3) Incidentally the properties of Hasbach's remarkable satellite systems had to be considered. It is shown that they are all related to the P(1) series lines, obey very closely displacement rules, and that they afford direct experimental evidence for the rules of link modification.

* 'Analysis,' p. 132. The values for Na, K, Rb, Cs also are 6^2+3, 7^2+4, 7^2, 7^2+2.

The Maps.

The maps contain the raw material for discussion. It is to be expected that a number of the separations given will not correspond to real links or L, M values, but will merely be numerical coincidences, and indeed the discussion shows that such are present and can be excluded as false or pseudo links. Such are included in [ ]. Doubtless some still remain but the proportion is probably small, for if there were a considerable proportion, the chains from one map should be expected to run on into another depending on a different series line. It is very remarkable that no such case occurs. In the maps a circle represents a line with an included number referring to an accompanying list giving the wave-lengths and wave-numbers. The small numbers outside a circle give the separations from the next lines on either side, so as to indicate the degree of crowding or the reverse in the spectrum. The important numbers for our present purpose are the separations in a chain, and these are given in block figures in the junction line between two circles. The wave-numbers increase in a chain from left to right, and when a link is drawn vertically the increase is downwards, unless an arrow is drawn in the opposite direction. The lists contain also the formulæ determined for a large number of the lines involved, especially where the L, M occur. These indicate the displacements required and also give the wave-number difference from the observed value, which should be less than the probable observation error. Unless this condition can be met without involving more than a few ouns displacement on the two terms entering, the link is regarded as a false one. Lines observed in R.A. are entered in italics. They are mostly spark lines by E.V.

Map I. P(1).

$P_2(1)=3273{\cdot}967,\ 30535{\cdot}217\ ;\ P_1(1)=3247{\cdot}550,\ 30783{\cdot}59.$

Oun shift on $s(1)=3{\cdot}43$.

The map contains the linkage from P(1) involving e, u, v.

1	2	3384·815	29535·26	$e.P_2-{\cdot}16$	$=e.P_2(-1)+2y-{\cdot}05$
2		8·55	16·06	$e.P_2.u+{\cdot}01$	} is sat. (7)
	8	3307·952	30221·51	..... $+10x+{\cdot}06$	
3	4	3235·712	30896·21	$e.P_2.2u-y+{\cdot}10$	
4	2	3233·89	30913·62	$e.P_2.u.v+10x+{\cdot}09$	

P(1) (*continued*).

5	4	3208·236[1]	31160·80	$e\,.\,P_1\,.\,u\,.\,v+10x-\ 2y-{\cdot}02$	is sat. (10)
		8·119	61·93	..... $-{\cdot}03$	
		7·94	63·69	..... $+\ 3y+{\cdot}02$	
		7·65	66·50	..... $+10y-{\cdot}02$	
6		80·687	72·67	..... $-\ 5x-y+{\cdot}06$	is sat. (9)
		80·40	75·34	..... $-y+{\cdot}03$	
	3	3279·823	30480·69	$e\,.\,P_1\,.\,v+10x-y-{\cdot}02$	
		9·54	83·33	..... $+15x-y-{\cdot}08$	
		9·06	87·78	..... $+23x-y+{\cdot}05$	
7	$3n$	3175·73	31479·75	$P_1\,.\,v+10x-2y-{\cdot}19$	
8	$6n$	3108·603[2]	32159·49	$(-2)P_1(-3)\,.\,u\,.\,v+0$	is sat. (12)
		8·43	61·55	$(-2)P_1(-3)\,.\,u\,.\,v+4x-{\cdot}10$	
9	$2n$	3014·84	33159·64	$(-1)P_1\,.\,e\,.\,u\,.\,v+{\cdot}10$	
10	2	3044·032	32841·64	$(-1)P_1(1)\,.\,2e\,.\,u\,.\,v+{\cdot}06$	
11	$1n$	3392·01	29472·61	$2e\,.\,(1)P_1\,.\,v-{\cdot}03$	
12	3	3572·136	28792·50	$2e\,.\,u\,.\,P_1(-1)\,.\,v-3y-0$	
13	3	3315·399	30153·63	$2e\,.\,P_1(-3)\,.\,u\,.\,v+y+{\cdot}07$	
14	$2n$	3354·475	29802·40	$e\,.\,u\,.\,(-1)P_1(-3)\,.\,v+0$	

In the P maps the satelloids introduce the unknown x, y shifts and in general they have been left in the lines linked to them.

[1] The first satelloid is 248·31 ahead of (4) or 248·40 of its formula, whilst the P_2, P_1 are separated by 248·37, so that we get here a change from P_2 to P_1.

[2] The map shows it is a $P_1\,.\,u\,.\,v$ line and direct calculation gives the displacements indicated in the formula.

Map II.

Annex to I. with X, L, M separations. For extensions from (12, 13) of I. see map VI.

1 is (6) of I and related to P_2. Hence 51·90 is a false M.

2	3	3268·278	30588·36	$P_2(b+2)-1{\cdot}72=P_2(b+2)-3y-{\cdot}01$

53·13 is excessive, but it is followed by an excessive −134·52 to (3) giving a more normal L–M. Moreover, the formula gives the value very exactly. We must suspect that (2) has a satelloid $3y$ less.

3		3·09	50·36	$(-1)P_2(\quad\quad)-{\cdot}02$	is sat. (8)
	4	3282·716	30453·84	$P_2(-a+b-1)+{\cdot}03$	
		2·33	57·42	$(+1)P_2(\quad\quad)+{\cdot}18$	

This satelloid set does not depend on y, but the seps. are

due to ± one oun displacement in $s(1)$. We note the symmetrical series inequalities in u from one and v from the other satelloid.

4	1	3358·76	29764·37	$v\,.(-1)P_2(-a+b-2)+y-\cdot12$
5	1*n*	3209·47	31148·83	$(-1)P_2(-a+b-2)+y+\cdot18$
6	1	3358·31	29768·36	$u\,.(1)P_2(-a+b-2)-\cdot14$
7	2*nb*	3211·44	31129·72	$(1)P_2(-a+b-2)\,.\,u-\cdot04$
8	2	3277·331	30503·88	$P_2(-a+2b-1)-\cdot05$
9	1*n*	3223·044	31017·64	$(-1)P_2(-2a+b-2)\,.\,v+y-\cdot15$
10	3*n*	3223·24	31014·00	$(-1)P_2(-2a+b-2)\,.\,v+y-3\cdot79$
i. e. is (9) displaced by 3 ouns =				$(-1)P_2(-2a+b-5)\,.\,v+y-\cdot01$
11	1*n*	3218·23	31064·04	$(-1)P_2(-2a+2b-5)\,.\,v+\cdot15$

A separation of 130·02 is shown as between $P_1(1)$ and (4) of I, linked to it. Hence 130·02 is a false L.

12	1*n*	3239·16	30863·32	$e\,.P_2(-b)u\,.\,v+9y+\cdot11$
	is 50·30 behind (4) of I =			$e\,.P_2\,.\,u\,.\,v+10y-\cdot21$
13	3*n*	3293·903	30350·42	$e(-1)P_1(-a)v-\cdot05$

This divides the separation between the linked (2) and (6) of I. Of the two L links represented, one at least is therefore false. Regarded as dependent on (6) of I, the formula reproduces the line exactly; if it depends on 2 of I (+128·91), the formula is $e(-1)P_2(a+1)+\cdot11$ outside O.E. This decides in favour of 130·27 being real.

14	4	3317·225	30137·04	$X_2\,.\,e\,.\,P_1(-a)v-2y-\cdot02$
15	3	3266·814	30609·57	$e\,.(-2)\,P_1(a-1)\,.\,v+0$
16	2	3252·22	30739·38	$e\,.(-2)\,P_1(2a+1)\,.\,v+\cdot13$
17		4·66	3·23	$e\,.(-2)\,P_1(a+1)\,.\,u\,.\,v+\ y+0$
		4·34	6·36	$\ldots\ldots\ldots\ (a+5)\ldots\ldots -2y-\cdot03$
	6	3194·103	31298·67	$e(-2)P_1(a+5)u\,.\,v+2y+0$
		3·979	9·89	$\ldots\ldots\ldots\ldots(a+6)\ \ldots\ +2y+0$
		3·81	301·35	$\ldots\ldots\ldots\ldots(a+7)\ \ldots\ +2y+\cdot23$

is sat. (11)

We come here to a false cycle, with at least one false L or M. Either the 129·54 is real, connecting (17) to (5) of I whose satelloid in question is $e\,.\,P_1\,.\,u\,.\,v+10x+3y+\cdot02 = e\,.\,P_1\,.\,u\,.\,v+7\cdot13$. In this case one at least of the L, M 129·80, 50·25 must be false, or the latter may be real and 129·54 false, or both sets false. On the first supposition the longest satelloid of (17) is $e\,.\,P_1\,.\,u\,.\,v+7\cdot13+129\cdot54$. Here $a+1$ on p_1 shifts 129·27 and we get $e\,.\,P_1(a+1)\,.\,u\,.\,v+7\cdot43 = e\,.\,(-2)\,P_1(a+1)u\,.\,v+y+0$. The main line is 5·44 larger, which is $4\delta_1$ on $p_1(a+1)+y+0$. This explains the failure of the y-multiple for the extreme satelloid in Table I. of the

satelloids. Also the first violet 1·22 with very exact measures is δ_1 on $p_1(a)$. The formula for the main is therefore as entered above. Not only therefore do we get exact formulæ with this separation as a real L, but the current term $p_1(a)$ entering enables us to explain the satelloid separations, a difficulty in discussing Table I.

18	6	3126·106	31979·44	$e\,.\,(-2)\mathrm{P}_1(a+5)2u\,.\,v+2y+\cdot14$ $=e(-2)\mathrm{P}_1(a+6)\,.\,2u\,.\,v+\cdot03$
19	2	3113·468	32109·24	$e\,.\,(-2)\mathrm{P}_1(2a+8)\,.\,2u\,.\,v+\cdot22$ *or* $(-2)\mathrm{P}_1(-b-3)\,.\,u\,.\,v-\cdot78$

This may be either 129·80 on (18) *or* −50·25 on (8) of I, which is $(-2)\mathrm{P}_1(-3)\,.\,u\,.\,v+0$. The resulting formulæ would be as entered. As $\cdot78=y+\cdot21$ both are equally probable or improbable according to the simplicity with which ·21 can be met. $p_1(3)-6\,y$ gives −·02 in the first and $p_1(-2)+4\,y$ gives −·02 in second—both artificial—contrasted with exact reproduction of the sep. 129·54 at (17). We cannot in this kind of reasoning, especially with the presence of y, get certainty, but the 129·80 and 50·25 are marked as false. This is sustained below under (31, 32).

20	1	3118·355	32058·91	27	2	3149·501	31741·90	
21	4*n*	3146·821	31768·94	29	2	3160·047	31635·98	
22	1*n*	3151·61	31720·66	30	6	3063·416	32633·84	sat. (15)
23	3	3156·623	31670·30			3·18	36·35	
24	4*n*	3169·680	31539 84	31	4	3128·692	31953·01	
25	3	3088·121	32372·79	32	2	3149·501	31741·90	
26	4	3128·692	31953·01					

Nos. (21...24) and (29) serve for evidence on the L, M origins. (21) is $\mathrm{X}_1\,.\,e\,.\,(-2)\mathrm{P}_1(a+6)\,.\,2u\,.\,v-y-\cdot01$. A displacement $-(a+4)$ on $p_1(a+6)$ shifts 132·94, the observed 132·96 to $(29)=\mathrm{X}_1\,.\,e\,.\,\mathrm{P}_1(7)\,.\,2u\,.\,v+\cdot12$; $-b$ on $p_1(a+6)$ shifts 49·15, so that (22) becomes $\mathrm{X}_1\,.\,e(-2)\mathrm{P}_1(a-b+6)2u\,.\,v+\cdot24=\mathrm{X}_2\,.\,e\,.\,(-2)\mathrm{P}_1(a-b+6)\,.\,2u\,.\,v-\cdot03$; $-(b+1)$ on $(a-b+6)$ shifts 50·51 and (23) becomes $\mathrm{X}_2\,.\,e\,.\,(-2)\mathrm{P}_1(a-2b+5)\,.\,2u\,.\,v+\cdot12$; and $-(a+1)$ on $a-2b+5$ gives 129·80 and (24) is $\ldots(-2b+4)\ldots -y+\cdot03$. All these support the displacement theory of L, M.

(31, 32) are the same as (27, 26), so that there is a cycle, viz. starting from (31), $u-e+\mathrm{L}-\mathrm{X}-u-\mathrm{L}+e+\mathrm{X}$ which annul, so that we get a true cycle. It is interesting to note that had we made the 129 at 17 false and included 129·8+50 between 18 and 8I, the links would not have annulled and the cycle would have been false.

Map III.

This map starts from two parallel sets to (8) and (10) of I, indicated at the top of the map. 8 I is $(-2)P_1(-3) . u . v+0$, or if cleared of displacements is $P_1 . u . v+3{\cdot}16$. Thus (1) is $P_1 . u . v+93{\cdot}22$ and (4) is $P_1 . u . v+155{\cdot}03$. Now $(2b-4)$ on p_1 shifts 93·62 and $3b+6$ shifts 155·06. Hence (1) is $P_1(2b-4) . u . v-{\cdot}40 = P_1(2b+5) . 2u+0$, correcting the two links $-X_2 . u$ to exact values. So also (4) becomes $P_1(3b+6) . u . v+{\cdot}05$.

1	4	3099·922	32249·55	$P_1(2b+5) . 2u+0$	
2	2*n*	3120·452	32037·37	$X_2 . P_1(2b+5) . 2u+{\cdot}09$	
3	6	3036·105	32927·38	..... $-5y+{\cdot}08$	sat. (16
		6·89	29·72	..... $-y+{\cdot}11$	
		6·84	30·26	$P_1(2b+5) . 3u+{\cdot}08$	
4	6	3093·993	32311·36	$P_1(3b+6) . u . v+{\cdot}05$	sat. (13)
		3·72	14·25	..... $+5y+{\cdot}04$	
5	4	3073·803	32523·58	$P_1(3b+6) . u . v . X_2+0$	sat. (14)
		3·704	24·62	.....$+2x-{\cdot}04$	
		3·53	26·35	.....$+5x+{\cdot}07$	
6	2*n*	3030·25	32991·00	$P_1(3b+5) . 2u . v+{\cdot}26$ within O.E.	
7	5	3010·840	33203·69	$P_1(3b+5) . 2u . v . X_2-y-{\cdot}01$	
8	3	3022·608 [1]	33074·43	$P_1(-a+3b+4) . 2u . v . X_1+y+{\cdot}01$	
9	3*n*	3021·56 [2]	33085·89	$P_1(-a+3b+4) . u . 2v . X_1+y-{\cdot}01$	
10		1·716	54·38	$P_1(-a+3b+4) . 3u . v . X_1-{\cdot}12$	
	6	2961·177	33760·53	$P_1(-a+3b+4) . 3u . v . Y_1+10y+{\cdot}04$	
		0·92	63·48	$P_1(-a+3b+4) . 3u . v . X_1+16y-{\cdot}14$	sat. (18)
11	1	2875·69	34764·10	$P_1(-a+3b+4) . e . 3u . v . X_2+17y+{\cdot}11$	
12	2*n*	2979·38	33554·22	$P_1(-a+3b+4) . 3u . v+17y-{\cdot}13$	
13	2	2998·384	33341·59	$X_2 . P_1(-a+3b+4) . 3u . v+16y+{\cdot}08$	
14	1*n*	2911·21	34339·95	$X_2 . P_1(-a+3b+3) . e . 3u . v+16y-{\cdot}13$	
15	4	3140·318	31834·72	$P_1(3b+6) . u . X_2+6y-{\cdot}02$	
16	2	3068·912	32575·37	$P_1(4b+8) . u . v Y_2+{\cdot}11$	
17	1*n*	2991·76 [3]	33415·42	$P_1(3b+6) . u . v . 2X_2-2y+{\cdot}03$	
13*a*	4	2997·363	33352·97	$Y_2 . P_1(b-1) . 3u . v-{\cdot}14$	sat. (17)
		7·13 [4]	55·57	$Y_2 . P_1(b+1) . 3u . v+0$	
12*a*	2*n*	2978·293	33566·51	$P_1(b-1) . 3u . v+{\cdot}84$	
18	1*n*	2985·88	33481·22	$X_2 . P_1(a+b+1) . 3u . v+y+{\cdot}06$	
19	1*n*	2982·77	33516·11	$P_1(-1) . 3u . v+{\cdot}21$	

[1] $-(a+1)$ on $3b$ shifts 129·13. Note $-a+3b+4=5\delta=\frac{1}{2}b$.

[2] The separation from (8) is exact $v-u$, i. e. one of the u is replaced by v.

[3] Note the series inequality $211{\cdot}73+212{\cdot}69=2(X_2-{\cdot}06)$.

[4] The line is 13·98 from (13), and the linkage therefore $X \mid 3u . v$. Direct calculation for the satelloid gives then the result entered. *Or* the main is $11{\cdot}38=v-u-{\cdot}07$ ahead of (13), *i. e.* the $3u . v$ in that is changed to $2u . 2v$. The three parallel sets in this map therefore depend on $P_1(b+1)$, $P_1(2b+5)$, $P_1(3b+6)$.

Map IV. S(2).

$S_1(2) = (10)\ 8092{\cdot}74, 12353{\cdot}36$; $S_2(2) = (10)7933{\cdot}20, 12601{\cdot}80$.
Oun shift on $s(2) = {\cdot}5856$.

Meggers' probable errors are inserted in brackets.

S_1.

1	2	8178·96	12223·13 (03)	$(a-2)\,S_1(-8)+{\cdot}05$
2	1	8216·22	12167·70 (04)	$(a+b+7)\,S_1-{\cdot}02$
3	3	7774·18[1]	12859·56 (01)	$(a+b+7)\,S_1\,.\,v-{\cdot}26$
4	1	7124·66	14031·89 (09)	$(1)S_1(-1)\,.\,e\,.\,u-{\cdot}07$
5	1	8187·90[2]	12209·78 (07)	Q
6	1	8680·08	11517·46 (06)	$v\,.\,Q-{\cdot}24$
7	2	8446·40	11836·11 (04)	$u\,.\,v\,.\,Q(-1)\,.\,e-{\cdot}19$
8	1	8273·53	12083·53 (06)	

[1] I see no way of meeting the $-{\cdot}26$, which occurs also in (6, 7). This line should possibly be excluded. The two neighbouring lines are (2)...5·41; (4)...1·98 or $n=...57{\cdot}52$; ...63·20 separated from (3) by $-2{\cdot}04$ and $+3{\cdot}64$, the latter being 3 ouns on the p_1 term.

[2] This is 13·90 ahead of (1) and is doubtless a S_1 relative. Call it Q. The last separation suggests a change from p_1 to p_2. If the 247·42 is wholly this change, p_1 must enter as $p_1(2b-10)$, that of (1) being $p_1(a-2)$, a displacement of $12b$.

$S_2(2)$.

1	2	8017·78[1]	12468·84 (03)	$(a-2)\,S_2(-10)+{\cdot}03$
2	1*n*	7000·02	14281·74 (10)	$(-1)\,S_2(-3)\,.\,e\,.\,u+0$
3	2*n*	6935·80	14413·97 (06)	$(-a-2)\,S_2(-2)\,.\,e\,.\,u+0$
4	4	6621·61	15097·90 (02)	$(-a-6)\,S_2(-5)\,.\,e\,.\,2u+{\cdot}03$
5	2*n*	6565·54	15226·84 (07)	$(-2a)\,S_2(4)\,.\,e\,.\,2u+{\cdot}06$
6	2	6285·125	15906·18	$(-2a+1)\,S_2(4)\,.\,e\,.\,3u+{\cdot}03$
7	1*n*	6233·793	16037·16	$(-3a-1)\,S_2(-2)\,.\,e\,.\,3u+{\cdot}01$
8	2*n*	6253·371	15986·95	$(-3a+b-2)\,S_2(-3)\,.\,e\,.\,3u+0$
9	1	6531·437	15306·34	$(-3a+b-2)\,S_2(-3)\,.\,e\,.\,2u+{\cdot}02$
10	1	6835·46	14625·58 (10)	$(-3a+b-1)\,S_2(-1)\,.\,e\,.\,u+0$
11	2*n*	6775·64	14754·68 (06)	$(-4a+b-2)\,S_2(-9)\,.\,e\,.\,u+{\cdot}01$
12	1*n*	6890·64[2]	14507·89 (02)	$(-4a+b-3)\,S_1(-3)\,.\,e\,.\,u+0$
	2	89·92	09·96 (06)	$(-4a+b-3)\,S_1(-1)\,.\,e\,.\,u-{\cdot}09$
13	5	6599·681	15148·06	$(-a-b-4)\,S_2\,.\,e\,.\,2u+{\cdot}08$
14	2*n*	6544·51	15275·77 (09)	$(-2a-b)\,S_2(2)\,.\,e\,.\,2u+{\cdot}09$
15	1*n*	6840·99	14613·74 (02)	$v(-3a+b-2)\,S_2(-4)\,.\,e\,.\,2u+{\cdot}06$
16	1*n*	6213·785	16088·80	$(-3a-b-2)\,S_2(-2)\,.\,e\,.\,3u+{\cdot}01$

[1] Also $(a)\,S_2(-6)-{\cdot}11$, but the residual is too large.

[2] Or more probably the $-$"a" link $+(1)$ on $p_1 = (-4a+b-1)\,S_1(-9)\,.\,e\,.\,u$ $+{\cdot}01-$link "a".

S(2) (*continued*).

17	4	6119·545	16336·57
18	1	6199·195	16126·66
19	2	6296·599	15877·20
20	2	6157·577	16235·66
	1	7·371	36·21
21	2	6427·564	15553·69
22	2	6039·798	16552·26
23	1*n*	6064·686	16484·34
24	2*n*	6045·846	16535·71
	2*n*	·085	37·79
25	4	6325·450	15804·78
26		6059·446[3]	16498·60
27	1*n*	6151·576	16251·51
28	2	6274·624	15932·80
29	2	6296·599	15877·20
	2	4·004	83·75
30	4	6243·125	16013·19
31	3*n*	6223·655	16063·28
32	2	5966·594	16755·34
33	0	6504·051	15371·02
34	1	6415·155	15583·78
35	3*n*	6146·834	16264·04
	3*n*	8·190	0·46
	4*rv*	7·310	2·73
36	2*n*	6127·729	16314·75
37	2*n*	6583·542	15185·20
38	2	6032·326[4]	16572·77
39	3	7039·34	14201·98 (04)
40	5*n*	6485·142	15415·61
41	5	6090·226	16415·21
42	2*n*	6506·142	15365·85
43	2	6230·734	16045·03
44	3	6251·316	15992·21
45	1	6150·135	16255·31
46	1	6452·287	15494·11
47	5*n*	6474·176	15441·72
48	2*n*	1·240	90·99
	2*n*	6060·860	16494·75
		59·449[3]	98·60
49	2*b*	6749·29	14812·28 (10)
50	1*n*	6404·050[5]	15610·80
	1*n*	1·427	17·21
	1	0·591	19·25
51	2	6135·585	16293·87

The lines to three decimals are by Aretz.

[3] "Heads of bands"—? analogous to satelloids.
[4] Separation taken from mean of (29).
[5] The separations are links $a-\cdot55$, $c-\cdot03$, $d-\cdot99$.

Map V. ($d'-p1$.)

$D'_{12}(1)=5700\cdot247, -17538\cdot24$; $D'_{11}(1)=5732\cdot364, -17439\cdot98$; $D'_{22}(1)=5782\cdot127, -17289\cdot88$.

Oun shifts on $d_2'=2\cdot3977$, on $d_1'=2\cdot3905$.

As the P lines do not enter, the x, y shifts are not admissible. The first back link from D'_{12} is $e-\cdot63$, and ·63 not being met by displacements is excluded, and the 48·12 to (2) is not therefore capable of being tested. The two lines are close parallels to two lines (24, 23) of the S(2) linkage (map IV.), and must really belong to it. There are in this map several false cycles. As an indication of connexions, we have the 248·23 between (4, 5). This doublet ν separation suggests a change between two p_1, p_2 terms. If (5) is connected to the D'_{12} through $47\cdot51-129\cdot63$, it depends on $-p_1$ and $+\nu$ cannot change to $-p_2$. We shall start therefore

in the opposite direction by the chain D_{11}, 3, 4, 5. The dashes in D′ are omitted.

1	2*n*	6045·085	16537·80	
2	1	6062·726	16489·67	false link
3	1*n*	*5663·52*	17652·53	$D_{11}.Y_2+·01$
4	1*n*	*5646·93*	17704·40	$D_{11}(b+2).Y_2+·10$
5	1	5727·063[1]	17456·12	$D_{21}(b+2).X_2-·05$
6	1*n*	*5685·03*[2]	17585·75	$D_{21}(a+b+2).Y_2+·05$ (see note)
7	1*n*	5631·65	17751·85	$D_{12}(1).X_2+·09$
8	3	*5679·42*	17603·12	$D_{11}(-b).Y_2+·07$
9	3	*5566·35*[3]	17960·71	$D_{12}.X_1.Y_2+·07$
10	1	5360·099[4]	18651·19	?
11	2*n*	*5668·77*[5]	17636·18	$D_{21}(a+2b+3).X_2+·01$
12	4*n*	*5652·16*	17688·02	$(-1)D_{21}(a+3b+3)X_2+·09$
13	4	*5438·79*[6]	18381·97	$e.D_{11}(-b-6).X_2.2Y_2.2u+·06$ (see note)
14	1*n*	*5453·93*	18330·93	$(1)D_{11}.Y_2.u+·20$ (within O.E.)
15	0*n*	5391·629	18542·12	$(1)D_{11}(-1).2Y_2.u+·05$
16	1*n*	5200·87	19222·22	$(1)D_{11}(-1).2X_2.2u+·06$
17	3*n*	5144·106	19434·32	$D_{11}(-3).3X_2.2u-·03$
18	1*n*	*5158·53*	19380·62	$D_{11}(-b-7).3Y_2.2u-·12$
19	1	*5130·97*	19484·72	$(-1)D_{11}(-b-4).3X_2.2u-·10$
20	1*n*	*5429·01*	18414·83	$D_{11}(-a-1).2X_2.u-·23$
21	2*n*	*5408·56*	18484·70	$e.D_{11}(b-5).3Y_2.2u+·03$
22	2*n*	5076·283	19693·98	$D_{11}(b-3).X_1.X_2.2Y_2.2u-·07$
23	0	5022·770	19903·82	$D_{11}(b-3).2X_1:X_2.2Y_2.2u-·07$
24	3	*5203·74*	19212·15	$v.D_{11}(b-3).2X_1.3Y_2.2u+·07$
25	2*n*	*5089·54*	19643·36	$D_{11}(-4).X_1.X_2.2Y_2.2u-·13$

[1] The 248 suggests $-\Delta$, or p_1 to p_2. But $-\Delta$ on p_2 $(b+2)$ shifts 247·83. Note, D_{21} is a "forbidden" line.

[2] This is 129·63 ahead of (5) and 47·51 of D_{12}, one link at least being false, For the former $+a$ on p_2 $(b+2)$ shifts 129·26. On this supposition the formula is as entered. Also b on p_1 shifts 49·31, and the formula based on D_{12} is $D_{12}(b-1)-·57$ and ·57 cannot be met by any simple displacements on d_2, p_1. This points to 47·50 as being the false one. This is supported by the next 50·43 link—see note 5 below.

[3] Note the series inequality $213·61+208·86=X_1+Y_2+·02$. This and (4) are so exact that the false link in this cycle must be either 690·48 or 998·66 to (10).

[4] On the two possible suppositions of linkage to (9) or (3), the first gives $D_{12}(-1).X_1.X_2.v-·05$, and the second $(1)D_{11}(1).Y_2.e+·03$. The measure is by Aretz with O.E. about ·05, so that it is not possible to decide which (if not both) is false. Both are marked doubtfully false.

[5] If based on (5) formula $= D_{21}(a+2b+3).X_2+·01$, if on D_{12} is $D_{12}(2b-1)+·63$. Thus line (11) supports (6) in making 47·50 false.

[6] The map shows three links: $v+1·87$ from $(12)=(-1)D_{21}(a+3b+4).X_2.e+·69$, and thus excluded; 51·04 from (14) gives $(1)D_{11}(b+1).Y_2.u+·70$, also excluded; whilst 998·65 from (18) gives that entered with residual ·06. The *e* link is thus not necessarily excluded.

This map is noticeable for the alternative succession of X links, especially the $X+u+X+u+X+M+X+X$.

Map VI. ($S_1(5)$ and P(1).)

$S_1(5)$, $(2n)$ 3598·01, 27785·25; $D_{11}(4)$, $(3n)$ 3687·5, 27110·9.

Oun shift on $s(5) = \cdot 0504$; on $d(4) = \cdot 0646$.

$S_1(5) - \cdot 05$ [1].

1	6	3599·135 [2]	27776·56	(7) $S_1 - 0$
2	$4n$	3512·122	28464·71	(1) $S_1(-1) . u - \cdot 01$
3	2	*3393·09*	29464·19	(1) $S_1(-1) . u . e - \cdot 33$
4	$2n$	*3688·60* [3]	27103·75	u . (1) $S_1 + \cdot 36$
		·38	05·37	$u . (-1) S_1 - \cdot 48$
5	$2n$	3695·73	27053·75	$u . (b+1) S_1 - \cdot 33$

[1] A probable correction.

[2] There is an analogous displaced line for $S_1(4) = (-7) S_1(4)$. The two separations are respectively $-8 \cdot 64$, $+8 \cdot 62$.

[3] The two measures are by K.R. and by Crew & Tatnall. The map takes the mean, but probably as indicated here they are $\pm$ one oun on the limit. The first (K.R.) shows the same displacement as the other lines and explains the M as a b displacement on (4).

The P portion.

(For general discussion see p. 218.)

1	$2n$	3624·236	27584·18	$X_2 . Q$	
2	2	3641·693	27451·96	$X_2 . (1) Q(-a) + \cdot 05$	
3	2	3648·385	27401·60	$X_2 . (1) Q(-a-b) - y + \cdot 02$	
4	2	3665·740	27271·89	$Y_2 . (1) Q(-2a-b) - y - \cdot 05$	
5	2	3734·23	26771·70	$u . Y_2 . (1) Q(-a) + \cdot 11$	
6	3	3741·247	26721·49	$u . X_2 . (1) Q(-a-b) - \cdot 03$	
7	2	3759·495	26591·78	$u . Y_2 . (1) Q(-a-b) - \cdot 09$	
8	3	3613·753	27664·19	(1) $Q(-a) + \cdot 01$	
9	2	3620·346	27613·83	(1) $Q(-a-b) - y - \cdot 02$	
10	1	3712·000	26932·02	u . (1) $Q(-a-b) - y - \cdot 20$	
11	$1n$	3676·37	27189·34	$2X_2 . (1) Q(-a-b) - y + \cdot 03$	
12	2	3659·358	27319·44	$2X_2 . (1) Q(-b) + y - \cdot 14$	
13	$1n$	3652·40	27371·48	$2Y_2 . Q + \cdot 11$	
14	2	3645·236	27425·27	$2Y_2 . (-1) Q(b) + 2y + \cdot 02$	
15	$1n$	3546·45	28189·19	$2X_2 . (1) Q(-a-b) . e - y + \cdot 08$	
16		0·67	15·18	$X_2 . Y_2$ ..... $(-b+1) . e - 8y - \cdot 01$	
		0·55	16·14	..... $(-b-1) . e - \cdot 09$	
	6	3530·388 [1]	28317·44	..... $(-b+1) . e - 4y - \cdot 03$	sat. (5)
		0·251	18·52	$X_2 . Y_2 . (1) Q(-b) . e + \cdot 01$	
		0·10	19·75	..... $(-b+1) \ldots + 0$	
17	4	3524·240	28366·83	$X_2 . Y_2 . (1) Q . e - 2y - \cdot 04$	
18	2	3517·029	28425·00	$2Y_2 . (-1) Q(b) . e + 2y - \cdot 03$	
19	4	3520·032	28400·75	$X_2 . (1) Q(-a-b) . e - 2y - \cdot 08$	

[1] Compare the discussion in Table I. The true linked line is here represented by the 1st viol. sat., the 2nd is an oun shift in p on this. The main and extreme red are respectively $4y$, $8y$ from the extreme violet, and the 1st red is a two-oun shift in p from the 1st viol.

20	1*n*	3435·53[2]	29090·81	$X_2 . (1) Q(-a-b) . e . v-2y+·07$
21	2	3498·063[3]	28579·09	$X_2 . 2e . u . P_1(-1) . v-5y+0$
22	1	3379·69	29580·05	$X_2 . e . u . P_1(-1) . v-3y+·02$
23	2*n*	3487·565	28665·14	$(1) Q(-a) . e+2y+·02$
24	3	3472·136	28792·50	$2e . u . P_1(-1) . v-3y+0$
25	1*n*	3392·01	29472·61	$2e . \quad P_1(-1) . v-4y+·05$
26	3	3315·399	30153·63	$2e . \quad P_1(-3) . v . u+y+·05$
26*a*	2	3292·392	30364·34	$\ldots\ldots\ldots . Y_1+2y-·02$
26*b*	2*n*	3404·66	29363·11	$e . \quad P_1(-3) . u . v . Y_1+·09$
27	4	3329·638	30024·70	$2e . P_1(-a-3) . u . v+y-·02$
28	3	3335·235	29974·30	$2e . P_1(-a-b-3) . u . v+·03$
29	6	3450·335	28974·42	$3e \ldots\ldots\ldots\ldots -·05$
30	4	3475·998	28760·52	$3e . X_2 \ldots\ldots\ldots -3y+·03$
31	2	3395·473	29442·54	$3e . X_2 . P_1(-a-b-2) . 2u . v-3y+·10$
32	1*n*	3420·16	29230·04	$3e . X_2 . Y_2 \ldots\ldots\ldots +·14$
33	2*n*	3404·66[4]	29363·11	$3e . X_2 . Y_2 . P_1(-b-2) \ldots\ldots +4·06$
34	2*n*	3331·13[4]	29567·45	$3e . X_2 . P_1(-b-2) \quad \ldots\ldots -4·14$
35	1	3341·184	29920·94	$3e . X_2 . P_1(-a-b-2) . 2u . 2v-5y+·06$
36	4*r*	3365·353	29706·06	$3e . X_2 . Y_2 \ldots\ldots\ldots -8y-·01$
37	1*n*	*3817·45*	26189·60	$e . 2X_2 . (1) Q(-a-b)-y+·09$
38	2	3720·770	26868·57	$e . 2X_2 . (2) Q(-a-b+1) . u+·05$
39	2*n*	3627·33	27560·65	$\ldots\ldots\ldots\ldots . u . v+·05$
40	2	3500·314	28560·72	$2X_2 . \ldots\ldots\ldots +·32$
41	1	3474·574	28772·30	$Y_2 . (2) Q(-a-b+2) . u . v+·04$
42	2*n*	3415·83[5]	29267·10	$X_2 . 2e . u . P_1(-1) . 2v-12y-·08$
43	3	3440·52	29057·08	$Y_1 . \ldots\ldots\ldots\ldots +·11$
44	2*n*	3465·4	28848·4	$X_1 . Y_1 . X_2 . 2e . u . P_1 . 2v-12y+·09$
45	4*n*	3349·287	29848·55	$2X_1 . X_2 . e . u . P_1 . 2v-12y+0$
46	1	3361·96	29736·01	$Y_1 . Y_2 . 2e . P_1(-2) . 2v-12y-·09$
47		8·45	45·44	$Y_2 . 2e . P_1(-5) . 2v-7y+·01$
		8·11	48·49	$Y_2 . 2e . P_1(-3) . 2v-6y+0$
		8·04	49·11	$\ldots\ldots\ldots\ldots -5y+·03$
	6	3337·850[6]	29950·82	$Y_2 . 2e . P_1(-3) . 2v-2y+·04$ } sat. (6)
		7·73	51·90	$X_2 . 2e . P_1(-1) . 2v-5y+·10$
		7·668	52·45	$\ldots\ldots\ldots\ldots -4y+·08$
		7·571	53·32	$Y_2 . 2e . P(-1) . 2v-2y+·08$

[2] E.H. give ... ·01, *n*=... 95·21. The double circle in the map denotes that the mean ... 93·01 is taken.

[3] This formula is deduced direct from (24). If from (17) it is $Y_2(1) Q . e -2y - ·05$ with $Q=3e . u . P_1 . v+·80$. They both reduce to $X_2 . 2e . u P_1 . v-4·09$.

[4] 133·07+124·91=2×128·99 and *a* on $(-a-b-2)$ shifts 129·15, so that these two lines show parallel inequality and are both displaced *a* on p_1 and equal and opposite 4·04, or $\pm 7y$ within errors.

[5] The link is $v-4·07$, the same displacement as in (33, 34); since $-12y = (2) s2+·02$ the formula may be $X_2 . 2e . u . (2) P_1(-1) 2v-·06$.

[6] This satelloid in Table I. was found not to be completely subject to the *y*-rule. It is now seen that the cases which fail are met by a change from X_2 to Y_2 and displacements on p_1.

The P portion (*continued*).

48	2	3610·806	27686·79	$X_2 . Y_2 . u . (1) Q . e - 3y + \cdot 02$
49	1	3629·794	27541·95	$X_2 . (-3) Q(-b-2) - y + \cdot 01$
50	1*n*	3721·70	26861·83	$X_2 . u (-3) Q(-b-2) - \cdot 05$
51	6	3602·038	27754·18	$(-3) Q(-b-2) - y - \cdot 03$ } sat. (4)
		1·75	6·39	.... $+3y - \cdot 10$ }
52	1*n*	*3664·21*	27284·16	$u . Y_2 . (1) Q(-a-b) . v - \cdot 11$
53	2*r*	3805·30	26271·71	$e . Y_2 Q(-2a-b-3) - y - \cdot 09$

$D_2(4)$ (2*n*, 3654·3, 27357·2).

I	2	3671·969[7]	27225·62	$(a+3) D_2 + \cdot 11$
II	1*n*	*3812·08*	26225·81	$e . (a+3) D_2 + \cdot 10$
III	2	3700·532	27015·48	$Y_1 . (a+3) D_2 + \cdot 18$

[7] The errors on these are all due to D_2, only measures to ·1. If it is $dn = \cdot 15$ greater ($d\lambda = -\cdot 02$) the errors are $-\cdot 04$, $-\cdot 05$, $+\cdot 03$.

Map VII. (D 2.)

Oun shift on $d(2) = \cdot 3035$.

$D_{12} = 19151 \cdot 63$ (Hasb.) $= \cdot 46$ (Aretz); $D_{11} = 19158 \cdot 370$;

$D_{22} = 19399 \cdot 838$ (Fabry & Buisson).

This map is connected with the D(2) lines. It comprises a short chain from D_{11} and a long one connecting D_{12} and D_{22}. The great majority of the lines are from the spark spectrum by Eder and Valenta, with possible O.E. of the order $dn = \cdot 15$ or over. As the oun shift in $d2$ is ·30, it is always possible to get within ·15 by a suitable choice of these $d2$ displacements, so that where such are involved with the spark lines we can draw no certain or definite conclusions. But some of the lines are much more exact, and conclusions may be drawn with more confidence, *e. g.* (4) in the D_{11} set excludes 681·20 as a real *u*-link if Aretz is reliable. A very long chain runs from D_{12} to D_{22} in which the links do not annul. There must therefore be at least one false link in it. Again, the line at (9) is a well-known line almost certainly not connected with D(2). It is numerically $D'_{12} . 3u + \cdot 99$, and if real involving $d_2' - p_1$. Shenstone gives reasons for introducing a new term, and treating it as $\phi - p_1$. The oun shift in $d_2' = 2 \cdot 398$ and in ϕ is 2·669. The parts of the map starting from D_{12} and from D_{22} show clear signs of being real, and the formulæ

are calculated for a number of lines from these. Also, the separations from (9) are considered as dependent on $D'_{12}\cdot 3u$ as well as on $\phi - p_1$,, with the result that the latter (Shenstone) and not the D' reproduces the links, and as lines near (9) have good measures the argument is good for the validity of ϕ, as well as for the link values.

If we look at the part from D_{22} back to (25), we recognize the chain to 31 as of normal aspect; then the chain of 4 successive X (25...39) is again a common effect and brings in (25) as a probable D(2) connexion. Again we notice the two parallel inequalities

$$\left.\begin{aligned} 1001{\cdot}64 &= e + 1{\cdot}84 \\ 210{\cdot}56 &= X_2 - 1{\cdot}71 \end{aligned}\right\} \text{from (25)},$$

$$\left.\begin{aligned} 678{\cdot}78 &= u - 1{\cdot}85 \\ 210{\cdot}69 &= Y_2 - 1{\cdot}85 \end{aligned}\right\} \text{from (35)};$$

also the two series inequalities in the long X sets from (25),

$$210{\cdot}56 + 214{\cdot}63 = 2Y_2 + {\cdot}10$$

$$\text{and} \quad 211{\cdot}08 + 210{\cdot}69 = 2Y_1 + {\cdot}08.$$

Since $(-1)\,D_2(2)$ shifts $1{\cdot}23 + {\cdot}60 = 1{\cdot}83$, we may feel safe in regarding the map between (25) and D_2 as dependent on $D_2(2)$. The formulæ have therefore been calculated for this part in the order D (2), 33, 32, 31, ...

Again starting from (9) = R (say R_1 if $\phi - p_1$, R_2 if $d_2' - p_1 + 3u$) for $-1000{\cdot}88 = -e - 1{\cdot}08$, $(-1)R_1(-3)$ gives $-1{\cdot}04$, $(1)R_2(1)$ gives $-1{\cdot}17$, in favour of R_1, but the O.E. may be considerable.

$-691{\cdot}84 = -v + {\cdot}24$ and (10) is $v(-1)R_1(-2) + {\cdot}04$ (Hasb.) or $+0$ (Aretz), and is not met by R_2. The O.E. is very small, so that R_1 is again good and R_2 impossible. $-212{\cdot}24 = -X_2 + {\cdot}03$ and (11) is $X_2 \,.\, v \,.\, (-1)R_1(-2) + {\cdot}07$ (or ·03). The O.E. is not large—see list.

D_{11}.

1	2	*5232·80*	19105·55	$(b+3)\,D_{11} + {\cdot}20$
2	3	*5268·38*	18976·51	$(a+b+4)\,D_{11} + {\cdot}12$
		$a+1$ on $b+3$ gives 128·96 close to observed sep:		
3	2*n*	*5282·34*	18925·86	$(a+2b+5)\,D_{11}(-1) - {\cdot}11$
4	1	5052·485	19786·741	$(b+3)\,D_{11}(2) \,.\, u + {\cdot}16$

D_{12}.

1	1	*5255·62*	19022·59	$(a+1)\,D_{12}+\cdot23$
2	1	*5270·13*	18970·21	$(a+b+3)\,D_{12}(-2)+\cdot08$
3	1*n*	5212·889	19177·89	$(a+b+5)\,D_{12}(-1)\,.\,X_1-\cdot13$
4	2	*5500·09*	18177·08	$e\,.\,(a+b+6)\,D_{12}(-1)\,.\,X_1+\cdot08$
5	(2)	*5563·83*,	17968·84,	6 (2*n*) *5357·27*, 18661·67, 7 (4) *5418·61*, 18450·41
8	3	*5380·75*	18580·24	$e\,.\,(-1)\,R_1(-3)-\cdot04$
9	3*n*	5105·543 F.B.	19581·115	$\phi-p_1\equiv R_1$ *or* $d_2'-p_1+3u\equiv R_2$
10	4	5292·539 H.	18889·281	$v\,.\,(-1)\,R_1(-2)+\cdot04$
11	2	5352·68 H.	18677·05	$X_2\,.\,v\,.\,(-1)\,R_1(-2)+\cdot07$
12	3	5554·94 H.	17997·01	$X_2\,.\,u\,.\,v\,.\,(2)\,R_1(5)+\cdot04$
13	3	*5389·70*	18549·39	$X_2\,.\,v\,.\,(-1)\,R_1(-a-1)+\cdot04$
14	3*n*	*5696·68*	17549·81	$X_2\,.\,v\,.\,(-2)\,R_1(-a)+\cdot06$
15	1*n*	*5338·19*	18728·38	20 3 *5608·83* 17824·68
16	1*n*	*5639·50*	17727·73	21 1*n* *5624·71* 17774·37
17	3*n*	*5574·10*	17935·73	22 3 *5666·62* 17642·91
18	2*n*	*5543·11*	18036·02	23 0 *5452·5* 18336
19	1*n*	*5760·40*	17355·41	24 2 *5456·02* 18323·90
25	4	*5495·12*	18193·52	$X_2\,.\,Y_1\,.\,u\,(2b+4)\,D_{22}(1)-\cdot06$
26	1*n*	*5440·90*	18374·83	
27	2	*5208·37*	19195·16	$X_2\,.\,Y_1\,.\,u\,(2b+3)\,D_2(3)\,.\,e-\cdot04$
28	1*n*	*5403·03*	18503·00	$X_2\,.\,Y_1\,.\,u\,.\,v\,.\,(2b+3)\,D_2(3)\,.\,e-\cdot12$
29	0*n*	5432·071	18404·07	$X_2\,.\,u\,(2b+4)\,D_{22}(2)-\cdot02$
30	1*n*	*5644·39*	17712·37	$X_2\,.\,u\,.\,v\,(2b+4)\,D_{22}(3)+\cdot06$
31	3	*5369·63*	18618·71	$u\,.\,(2b+2)\,D_{22}(2)-\cdot10$
32	1*n*	*5355·10*	18669·24	$u\,.\,(b+1)\,D_{22}(2)-\cdot03$
33	1*n*	*5340·71*	18719·54	$u\,.\,D_{22}(+1)+\cdot04$
34	4*n*	*5317·60*	18800·89	$u\,.\,(-a+b-1)\,D_{22}-\cdot03$
35	2	*5309·41*	18829·79	$u\,.\,(2b+3)\,D_{22}(2)\,.\,X_2-\cdot06$
36	1*d*	*5124·70*	19508·57	$(2b+4)\,D_{22}\,.\,X_2-\cdot09$
37	2	5111·945[1] H.	19556·59	$(b+5)\,D_{22}\,.\,X_2-\cdot05$
38	2	*5295·71*	18878·57	$(b+3)\,D_{22}\,.\,X_2-\cdot49$
39	0*n*	5250·511	19040·48	$u\,.\,(2b+4)\,D_{22}\,X_2\,.\,Y_2-\cdot08$
			or	$u\,.\,(2b+4)\,D_2(-1)\,.\,2Y_2-\cdot05$

F. B. = Fabry and Buisson. H. = Hasbach. Lines in italics are sparks by Eder and Valenta. The others by Aretz.

[1] The map is in error, the links being 48·02, 678·02.

Map VIII. (S3.)

$S_1(3)$, $6r$, 4530·843, 22064·79; $S_2(3)$, $6r$, 4480·376, 22313·32.

Oun shift on $s(3) = \cdot 203$.

These two linkages give the raw material, but the immediate separations from the S_1, S_2 are clearly no L, M. This cuts off the others, (4) excepted, from S connexions. This is also supported by the facts that (5, 7) are satelloids.

1	4*n*	4539·70	22021·64
2	1*n*	4513·20	22151·04
3	6*n*	4378·2	22834·0
4	6*n*	4674·76	21385·50
5	6	4704·598[1]	21249·87
		4·20	51·67
6	1*n*	4507·5	22179·0
7		2·30[2]	88·75
		1·986	90·20
	8	4651·130	21494·15
		0·73	96·00
		0·3	97·98
8	4	4509·386	22169·77
9	4*n*	4697·490	21282·03
10	1*n*	4500·37[3]	22214·18
11	2*n*	4642·6	21533·6
12	2*n*	4794·0	20853·6
13	1	4843·37	20640·95
14	2	4797·042	20840·37
15	2*n*	4767·5	20969·5

[1] Is sat. (1). [2] Is sat. (2).

[3] The separations (10 to 13) are exact Y_2, 680·11, 680·63 within O.E, and $693 \cdot 25 = v + 2y$.

The two satelloid sets point to the portions connected with them being P related. The main of (5) and the extreme violet of (7) are separated by 248·11 or the doublet ν within error limits. This suggests that (5) depends on p_2 and (7) on p_1, but their wave numbers as well as those of sat. (3) are so far below the others that any connexion is not evident.

Map IX. ($d_2' - p_1 2 \equiv$ R.)

Oun shift on $p(2) = \cdot 3241$, on $d_2' = 2 \cdot 398$.

1	8	2766·388	36137·57	4	2*n*	2782·61	35926·89
2	10*r*	2618·381	38180·16	5	2*n*	2786·52	35876·49
3[1]	1	2627·37	38049·61	6	1	2866·19	34878·10

[1] The 130·61 must be a spurious L if the allocation of R is correct.

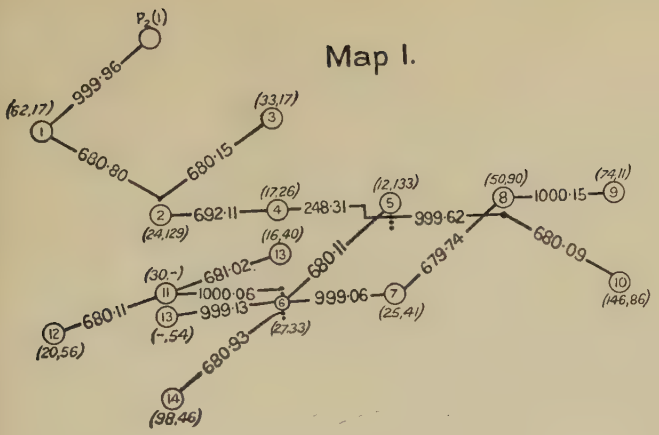
Appendix.

Table A. of shifts on p_1, p_2.

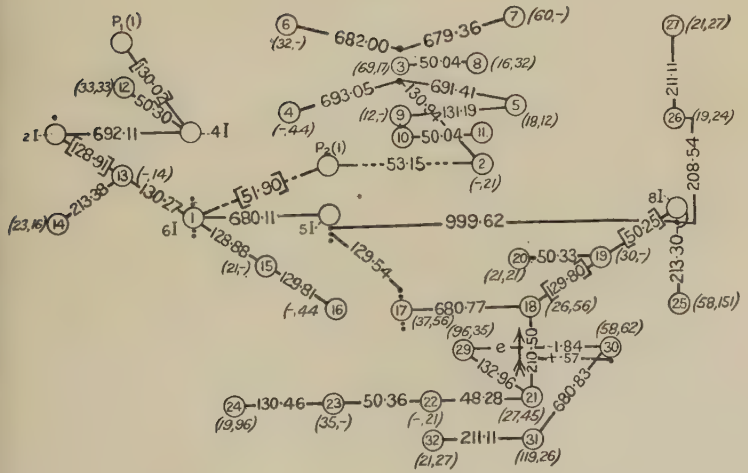
On p_1.	p.		Shifts per oun.	On p_2.
$2a$	31269·24		1·2199	
$4b$	327·90		1·2234	
$a+b$	347·46		1·2246	
$3b$	376·89		1·2262	
a	396·48		1·2274	
$2b$	425·99		1·2291	
b	475·22		1·2320	
0	524·53	p_1	1·2349	$5b$
$-b$	574·00		1·2378	$4b$
	593·81		1·2390	$a+b$
$-2b$	623·54		1·2407	$3b$
	643·41		1·2419	a
$-a$	653·37		1·2425	
$-3b$	673·27		1·2437	$2b$
$-a-b$	703·13		1·2454	
$-4b$	723·08		1·2466	b
$-5b$	772·97	p_2	1·2495	0
$-6b$	823·02		1·2525	$-b$
	873·21		1·2554	$-2b$
	903·36		1·2572	$-a$
	923·47		1·2584	$-3b$
	953·70		1·2602	$-a-b$
	973·87		1·2614	$-4b$
	32024·40		1·2644	$-5b$
	034·54		1·2650	$-2a$
	075·01		1·2674	$-6b$
	125·79		1·2704	$-7b$
	166·52		1·2728	$-3a$
	176·66		1·2734	$-8b$
	227·67		1·2765	$-9b$
	278·80		1·2795	$10b$
	299·26		1·2807	$-4a$
	432·89		1·2887	$-5a$

March, 1926.

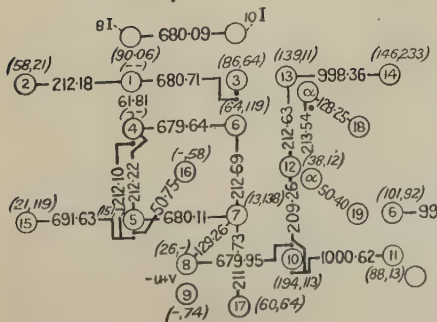
Map I.



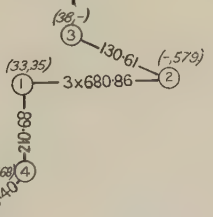
Map II.

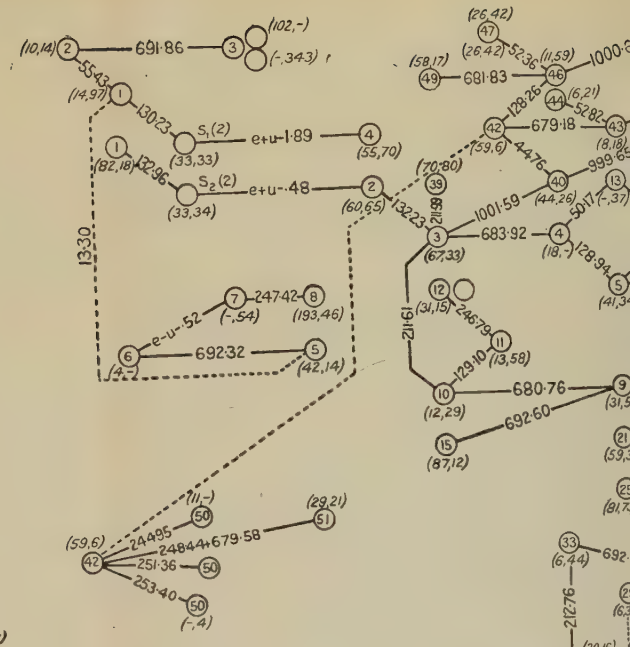


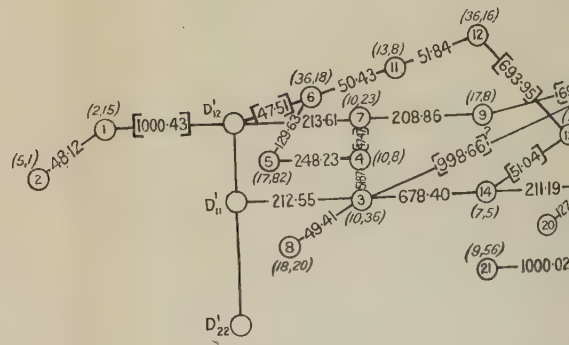
Map III.

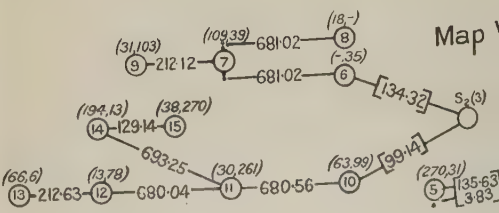


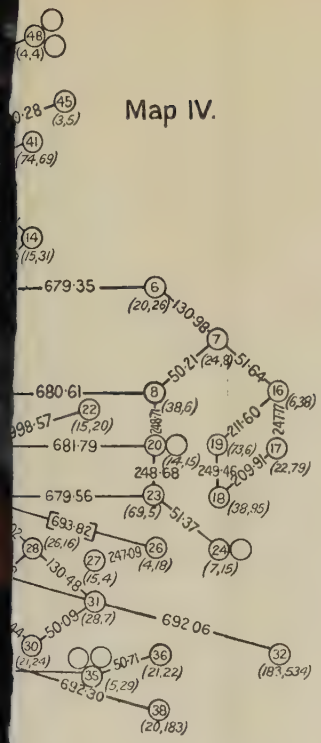
Map IX.

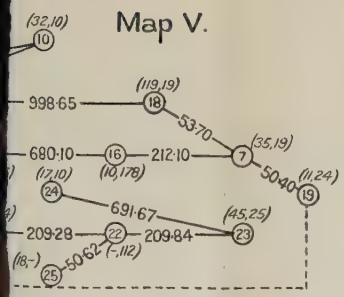


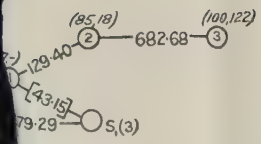


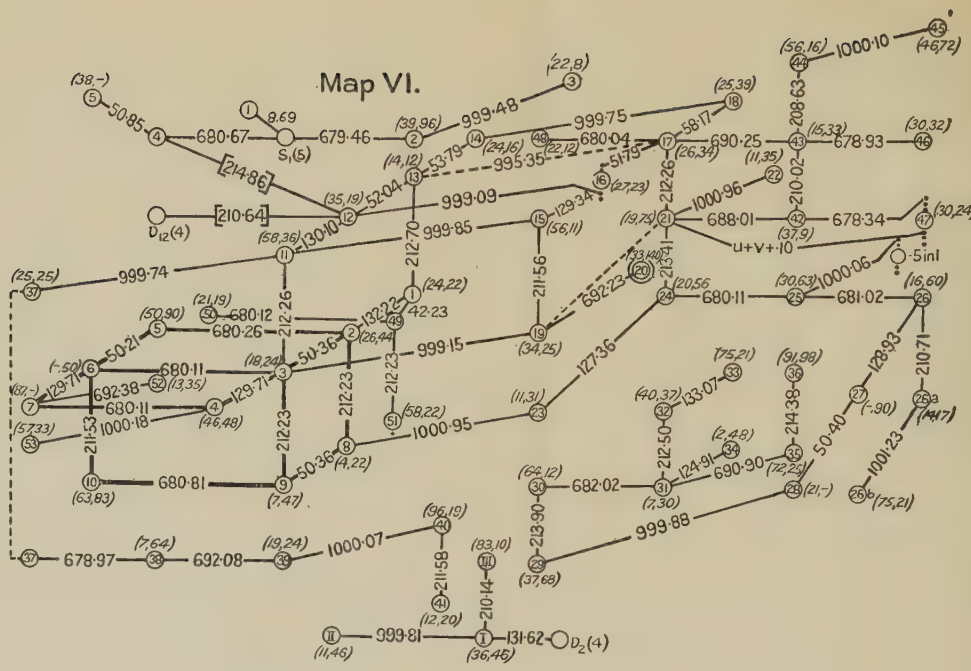


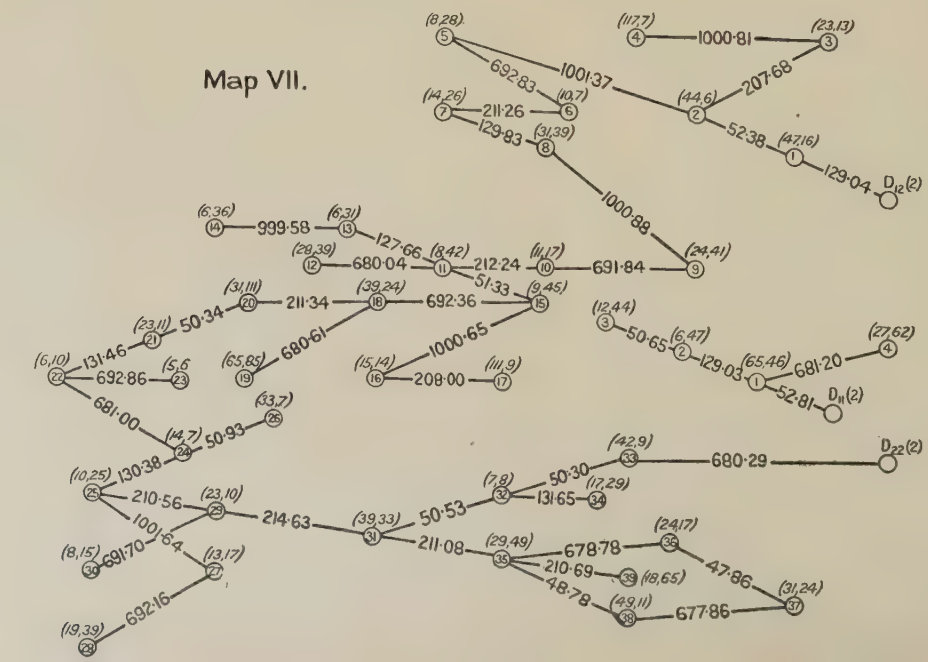



Map IV.


Map V.




Map VI.


Map VII.

XV. *Fluctuation Theory of Scattering of Light in Gases.* By Jakob Kunz, *Ph.D.**

IN a previous article published in this Journal † I have given an elementary theory of the scattering of light by small dielectric spheres. We can consider, however, the phenomenon of scattering of light by the molecules of a gas due to fluctuations of the density of the gas from point to point. It is the purpose of this article to show that the theory of fluctuations can be reduced in part to the previous theory, in which I used essentially the Stokes-Thomson method of determining the radiation of an oscillating charge.

As in the previous article, I assume a plane polarized light-wave proceeding in the z direction.

$$E_x = E_0 \sin 2\pi n\left(t - \frac{z}{v}\right) \quad . \quad . \quad . \quad . \quad (1)$$

through a gas of dielectric constant k. If k were constant we should have a wave of polarization so that

$$P_x = \frac{k}{4\pi} E_x \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

without scattering. If, however, k varies from the molecules to the vacuum, then we have instead of (2),

$$P_x = \frac{k+\Delta k}{4\pi} E_x. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We can now reduce the present case to the previous one if we add to it a virtual polarization

$$P_v = \frac{\Delta k}{4\pi} E_x. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In other words, if we add to the variable medium a polarization $-P_v$, then the scattering due to the heterogeneous state of the medium will be suppressed. We have, therefore, only to calculate the scattering due to P_v, acting in the volume element $d\tau$ and producing a displacement x in the charge of

* Communicated by the Author.
† Phil. Mag. xxxix. p. 416 (1920).

unit volume. If the charge contained in $d\tau$ is e, then we have

$$P_v = \frac{e}{d\tau} x = \frac{\Delta k}{4\pi} E_x, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or the displacement

$$x = \frac{\Delta k}{4\pi} \frac{d\tau}{e} E_0 \sin 2\pi t_n ; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

hence the acceleration

$$f = \frac{d^2x}{dt^2} = -\frac{\Delta k \, d\tau E_0}{4\pi e} (2\pi n)^2 \sin 2\pi nt. \quad . \quad . \quad (7)$$

We assume, further, that the volume element $d\tau$ contains $\nu = N \, d\tau$ molecules, where N is the number of molecules per unit volume. Moreover, we may assume that the small dielectric constant k can be expressed by

$$k = 1 + \alpha N = 1 + \alpha \frac{\nu}{d\tau},$$

denoting by α a constant ; then we get

$$\Delta k = \alpha \frac{\Delta \nu}{d\tau}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It has been shown by Sir J. Larmor that the energy radiated by the oscillating charge e per unit time is equal to

$$E_2 = \frac{2}{3} \frac{e^2 f^2}{V^3}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where V is the velocity of light in the dielectricum k, hence the energy radiated in the time interval dt becomes :

$$dE_2 = \frac{2}{3} \frac{\pi^2}{V^3} E_0^2 \, \Delta k^2 \, d\tau^2 \, n^4 \sin^2 2\pi nt \, dt,$$

and per unit time

$$E_2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \, \Delta k^2 \, d\tau^2 \, n^4. \quad . \quad . \quad . \quad . \quad (10)$$

Substituting (8) in (10) we obtain

$$E^2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \, \Delta \nu^2 n^4 \alpha^2,$$

but $\alpha = \frac{k-1}{N}$, hence

$$E_2 = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N^2} \Delta \nu^2 n^4,$$

and on average

$$\overline{E_2} = \frac{1}{3} \frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N^2} n^4 \overline{\Delta \nu^2}.$$

A fundamental theorem of the theory of fluctuations states that

$$\overline{\Delta\nu^2} = \nu = N d\tau,$$

hence

$$\overline{E_2} = \frac{1}{3}\frac{\pi^2}{V^3} E_0^2 \frac{(k-1)^2}{N} n^4 d\tau. \quad . \quad . \quad . \quad (11)$$

From Poynting's theorem it follows that the energy which flows through unit cross-section per unit time, E_1 is equal to

$$E_1 = \frac{E_0^2 V}{8\pi},$$

or

$$E_0^2 = \frac{8\pi E_1}{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Substituting (12) in (11) we obtain

$$\overline{E_2} = \frac{8}{3}\pi^3 \frac{E_1}{V^4} \frac{(k-1)^2}{N} n^4 d\tau,$$

but $n = \frac{V}{\lambda}$,

$$\overline{E_2} = \frac{8}{3}\pi^3 E_1 \frac{(k-1)^2}{\lambda^4 N} d\tau.$$

By Maxwell's theory of light, the index γ of refraction is equal to $\sqrt{k}$ or $k-1 = \gamma^2 - 1 = 2(\gamma-1)$ approximately, hence

$$\overline{E_2} = \frac{32}{3}\pi 3 \frac{E_1(\gamma-1)^2}{\lambda^4 N} d\tau.$$

This is the light energy diffused per unit time from the volume $d\tau = d\mathrm{S}\, dz$. This scattered energy corresponds to the difference of the energy which flows in the primary beam through the cross-sections $d\mathrm{S}$ and $d\mathrm{S}'$, hence

$$\frac{dE_1}{dz} = -\frac{32}{3}\pi^3 \frac{E_1(\gamma-1)^2}{\lambda^4 N} d\mathrm{S},$$

and per unit cross-section

$$\frac{dE_1}{dz} = -\frac{32}{3}\pi^3 E_1 \frac{(\gamma-1)^2}{\lambda^4 N} = -hE_1,$$

or

$$\log E_1 = \log E_0 - hz,$$

or

$$E_1 = E_0 e^{-hz}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where

$$h = \frac{32}{3}\pi^3 \frac{(\gamma-1)^2}{\lambda^4 N} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

is the famous coefficient first determined by Lord Rayleigh.

We proceed next to the consideration of a mixed gas whose dielectric constant $k=k_1+k_2-1$, where k_1 and k_2 are the corresponding constants of the two pure gases. If the number of molecules of the two gases in the mixture are n_1 and n_2 per unit volume and the volumes of the molecules v_1 and v_2 respectively, then by Clausius's theory we may write

$$k = 1+3n_1v_1+3n_2v_2,$$

$$\Delta k = 3v_1\Delta n_1+3v_2\Delta n_2,$$

or

$$\Delta k = 3v_1\frac{\Delta\nu_1}{d\tau}+3v_2\frac{\Delta\nu_2}{d\tau},$$

then we obtain from (10)

$$d\mathrm{E}_2 = \frac{1}{3}\frac{\pi^2}{\mathrm{V}^3}\mathrm{E}_0{}^2(3v_1\Delta\nu_1+3v_2\Delta\nu_2)^2n^4, \quad . \quad . \quad (15)$$

but

$$k_1 = 1+3n_1v_1,$$

$$k_2 = 1+3n_2v_2;$$

hence

$$d\mathrm{E}_2 = \frac{1}{3}\frac{\pi^2}{\mathrm{V}^3}\mathrm{E}_0{}^2\left(\frac{k_1-1}{n_1}\Delta\nu_1+\frac{k_2-1}{n_2}\Delta\nu_2\right)^2n^4,$$

and on an average

$$\overline{d\mathrm{E}_2} = \frac{1}{3}\frac{\pi^2}{\mathrm{V}^3}\mathrm{E}_0{}^2\left[\left(\frac{k_1-1}{n_1}\right)^2\overline{\Delta\nu_1{}^2}+2\frac{(k_1-1)(k_2-1)}{n_1n_2}\overline{\Delta\nu_1}\,\overline{\Delta\nu_2}\right.$$
$$\left.\mp\left(\frac{k_2-1}{n_2}\right)^2\overline{\Delta\nu_2{}^2}\right]n^4.$$

For a given value $\Delta\nu_1$ we have on an average a positive or negative value $\Delta\nu_2$ with the same probability; hence the double product vanishes, and

$$\Delta\nu = \Delta\nu_1+\Delta\nu_2,$$

$$\overline{\Delta\nu^2} = \Delta\nu_1{}^2+\Delta\nu_2{}^2 = \nu_1+\nu_2 = r,$$

by the theorem of fluctuations, mentioned above. $\Delta\nu_1$ and $\Delta\nu_2$ are small numbers. A solution of the last equation is given by

$$\overline{\Delta\nu_1{}^2} = \nu_1 = n_1d\tau,$$

$$\Delta\nu_2{}^2 = \nu_2 = n_2d\tau,$$

hence

$$\overline{d\mathrm{E}_2} = \frac{1}{3}\frac{\pi^2}{\mathrm{V}^3}\mathrm{E}_0{}^2\left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)^2}{n_2}\right]n^4\,d\tau,$$

and by (12)

$$\overline{d\mathrm{E}_2} = \frac{8\pi^3}{3}\frac{\mathrm{E}_1}{\mathrm{V}^4}\left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)^2}{n_2}\right]n^4\,d\tau,$$

or

$$\overline{d\mathrm{E}_2} = \frac{8\pi^3}{3}\mathrm{E}_1\left[\frac{(k_1-1)^2}{n_1}+\frac{(k_2-1)_2}{n_2}\right]\frac{1}{\lambda^4}\,d\tau.$$

Again,

$$k_1-1 = 2(\gamma_1-1)\,;\quad k_2-1 = 2(\gamma_2-1)\,;$$

$$\overline{d\mathrm{E}_2} = \frac{32\pi}{3}\mathrm{E}_1\left[\frac{(\gamma_1-1)^2}{n_1}+\frac{(\gamma_2-1)^2}{n_2}\right]\frac{1}{\lambda^4}\,d\tau.$$

From this expression we deduce the coefficient h as before :

$$h = \frac{32\pi^3}{3}\left[\frac{(\gamma_1-1)^2}{n_1}+\frac{(\gamma_2-1)^2}{n_2}\right]\frac{1}{\lambda^4}.$$

This theory leads to the result that the light scattered in a direction at right angles to the primary beam should be completely polarized, because we have considered the molecules as spherical and isotropic particles. But it is well known that even in the case of gases the transversely scattered light is imperfectly polarized. This imperfectness of polarization we may ascribe, with C. V. Raman *, to the anisotropy of the molecules with varying orientations.

XVI. *On the relation to Physics of the notion of Convergence of Series.* By Harold Jeffreys †.

ENOUGH work has been done on asymptotic and other divergent series to prove that an infinite series may be useful in physical applications without being convergent in the sense defined in works on pure mathematics. It is less generally realized that the converse is equally true, that a series may be convergent and yet be totally useless for the purpose of calculating the value of the function represented. For instance, the exponential series for e^{-1000} is convergent in the mathematical sense ; but it cannot be used to evaluate the quantity it denotes, for its terms increase rapidly up to the thousandth, which would have to be evaluated to over 870 significant figures, a quite unpracticable number.

The fact is that convergence and utility are not the same thing, and are essentially unconnected. In evaluating a function one is limited to expansions that can be actually

* C. V. Raman, Phil. Mag. xlv. p. 213 (1923).

† Communicated by the Author.

summed numerically in the time available, and it is therefore necessary that the first few terms shall give a good approximation to the function. These terms once obtained, the rest of the series is of no further interest to the physicist. The mathematical definition of convergence, on the other hand, depends on whether the sum S_n of the first n terms tends to a finite limit as n tends to infinity, and the criterion for the existence of such a limit depends only on the later terms.

The distinction recalls that arising in the theory of scientific inference in connexion with the possibility of a deductive theory not involving the notion of probability *. Deductive theories of scientific knowledge are usually based on the notion of infinite classes of data, or on that of a limit, which again implicitly involves infinite classes. Hence they are inapplicable to actual knowledge, which is necessarily in point of fact based on a finite number of data. The summation of a series, in the mathematical sense, could be carried out only by a being with infinite time at his disposal.

The definition of an asymptotic approximation, indeed, is nearer to the physicist's needs than is that of convergence. Such a definition is † that a series S is an asymptotic expansion of a function $f(z)$ if for all values of n

$$\lim_{z\to\infty} |\, z^n\{f(z)-S_n(z)\}\,| = 0.$$

The definition emphasizes the importance of the early terms of the series, and it is on the possibility of evaluating these that the usefulness of the expansion depends. It still, however, involves the notion of a limit when z tends to infinity; the physicist is concerned rather with the actual values of $f(z)$ and $S_n(z)$ for finite values of z, and needs more a specification of some value not exceeded by $|z^n\{f(z)-S_n(z)\}|$ within the range of values of z that he contemplates ‡.

A similar point arises in relation to certain series ordinarily regarded by the pure mathematician as slowly convergent. For instance, the exact sum of the series $\sum_{n=1}^{\infty} n^{-4}$ is known to be $\frac{1}{90}\pi^4$, or 1·081. The sum of the first four terms is 1·079, so that an accuracy of about 0·2 per cent. is achieved by taking only four terms. The series is usually considered slowly convergent because the ratio of consecutive terms tends to unity when n tends to infinity, but for physical purposes the rapid decrease of the early terms makes the series a very useful approximation.

* Wrinch and Jeffreys, Phil. Mag. xlii. pp. 369–390 (1921).

† Whittaker and Watson, 'Modern Analysis,' 8.2.

‡ *E. g.*, Whittaker and Watson point out that $n!/z$ is such a quantity in an illustrative example given by them.

The belief that convergence has something to do with physical utility may have arisen from the fact that the simplest series possessing either property are geometrical series, which are accordingly prominent in all discussions of both properties. But it is easy to find series possessing either property without the other, and it is well to specify as clearly as possible which one is being considered.

A further point of some importance is that a finite number of terms may be a good approximation to a function without being also a set of terms from a series of terms of the same form that represents the function exactly. The question has arisen in connexion with an approximate solution by Stoneley * of the problem of the straining of the earth by bodily forces. The stresses everywhere must be continuous, but as there is a discontinuity of the elastic properties at an internal layer the first derivatives of the displacements must be discontinuous. In principle, apart from matters peculiar to the special problem, the method has been to find two polynomials of the sixth degree in the distance from the centre such that the energy is a minimum for small variations in the coefficients. The actual state of equilibrium being such as to make the energy a minimum, the success of the method depends on the possibility of representing the displacement with sufficient accuracy by a polynomial of the assumed degree. As this is precisely the principle of ordinary interpolation, there seemed to be little doubt on the point until it was found that in the solution the coefficients of the terms of higher degrees were very much the greatest, making it clear that the polynomial was not the beginning of a convergent power series. It was, indeed, demonstrable *a priori* that the exact solution could not be expressed as a convergent power series, for such a series has a continuous differential coefficient at every point within its circle of convergence, whereas the solution in Stoneley's problem had a first derivative discontinuous at one point.

An analogue involving the same principle in a simpler form is provided by the electrostatic problem, in one dimension, of two plates at $x=\pm 1$, at potentials 0 and 1 respectively, the medium having dielectric constant 1 between $x=-1$ and $x=0$, and 2 from $x=0$ to $x=1$. The exact solution is easily found to be

$$V=\tfrac{2}{3}(1+x) \qquad -1<x<0$$
$$V=\tfrac{2}{3}+\tfrac{1}{3}x \qquad 0<x<1.$$

Now since V within the range considered is a function

* M. N. R. A. S., Geoph. Suppt. i. (1926).

with limited total fluctuation it is necessarily expressible over the whole range as a convergent series of Legendre polynomials in x. It follows that a solution to any required degree of accuracy can be found by taking enough terms of this series. But the sum of a finite number of polynomials can be rearranged as a single polynomial. Hence a solution to any degree of accuracy can be obtained as a polynomial, and the fundamental hypothesis of Stoneley's method is justified. But the coefficients of the same power of x in successive approximations do not tend in the limit to equality with the terms of a convergent power series; or indeed to any limit at all. If we assume

$$V = \sum_{n=0}^{\infty} A_n P_n(x),$$

we find by the usual methods

$$A_0 = \tfrac{7}{12}\,;\ A_1 = \tfrac{1}{2},$$

and for later terms,

$$A_{2m-1} = 0\,;\ A_{2m} = -\frac{4m+1}{6\,.\,2^{2m}}\,\frac{(2m-2)\,!}{(m+1)\,!\,(m-1)\,!}.$$

On applying Stirling's approximation we find without difficulty that when m is large A_{2m} is nearly $-\dfrac{1}{6\sqrt{\pi}}\,m^{-\frac{3}{2}}$. The Legendre functions never exceed unity, and the series therefore converges. Also its terms decrease rapidly at the beginning and steadily thereafter, so that it provides a useful approximation. A_6 is $-13/768$ and A_8 nearly $-0{\cdot}01$; the error in stopping at P_6 is therefore of the order of one or two per cent. The error of a polynomial approximation including x^6 will of course be the same.

But the coefficient of x^n in P_n is $(2n)\,!/2^n(n\,!)^2$, which is, by Stirling's approximation, equivalent to $2^n/\sqrt{(\pi n)}$. If we stop at x^{2m}, the coefficient of the highest power of x retained will be asymptotically equivalent to $2^{2m-\frac{3}{2}}/3\pi m^2$, which increases indefinitely with m.

The large values found by Stoneley for the later coefficients in his polynomials are therefore inherent in the form of approximation adopted, but do not thereby imply that the approximation is unsatisfactory. The polynomials are not correctly regarded as the beginning of power series, but as the rearranged early parts of Legendre series, which must be convergent and also suitable for computation. It is true, of course, as is pointed out by Stoneley, that the large later coefficients must be computed with the full absolute accuracy required for the earlier ones, but this is a matter of convenience and had to be weighed against others.

XVII. *Professor Lees' Criticism of 'The Surface History of the Earth.'* By Prof. J. Joly, *M.A., D.Sc., F.R.S.**

IN his review of my book (Phil. Mag. April 1926) Professor Lees sets forth certain difficulties which he says have to be overcome before the general theory involved can be accepted.

"One of these (difficulties)," he says, "is the concentration of the surplus heat from radioactive changes in a particular layer." If I apprehend Prof. Lees' objection rightly, the answer is that such a concentration forms no part of my theory. On the contrary, care is taken to guard against such an inference. I say (pp. 76–78): "It seems probable from these facts (*i. e.* the lesser radioactivity of the ultrabasic rocks and the very feeble radioactivity of meteorites) that the radioactivity of the Magma is succeeded by the lesser radioactivity of an ultrabasic layer which may reach to a depth of several hundred miles from the earth's surface. Further down the great core of the earth probably possesses much smaller quantities of the heat-producing elements. But this is surmise." The intervention of deep-seated radioactive heat at long intervals in connexion with certain major revolutions is also referred to not only in my book but in all I have written upon the subject. And, of course, the development of heat in the continental layer is frequently referred to. In a word, it is a leading feature of the theory that the arbitrary distribution of the radioactive elements is not only unnecessary but would give rise to difficulties. And this fact constitutes one of its claims to credibility.

After making this objection Prof. Lees immediately continues: "and another the secular rise of temperature of the earth during the whole of its past history owing to the amount of radioactive material postulated."

Upon this point I say (p. 76):—"If the natural question be asked:—'Does this source of heat also extend into the interior'?—we must answer that such evidence as we possess suggests an interior resembling the nickeliferous iron of the meteorite. Meteoric iron sometimes contains a minute trace of radium and therefore of uranium. The thorium content of metallic meteorites has not been investigated." This is the amount of interior radioactivity postulated.

Is there any difficulty raised here that does not affect any conceivable theory of earth-history based upon the facts at

* Communicated by the Author.

our disposal? We are up against the unknown and unknowable. But I think we would justifiably infer that the earth may be too young—even according to the greater estimates of geological time—to reveal any surface effects arising out of so feeble an interior radioactivity; and it is with its surface history that we are concerned.

Professor Lees continues: "The author unfortunately bases his calculations of the expansion in melting of the rocks 70 miles below the surface on the 10 per cent. increase of volume found when rocks melt at atmospheric pressure," etc.

This, however, is not the case.

The figures quoted are used in an early paper of mine (Phil. Mag. June 1923). The 10 per cent. expansion is not supposed to occur 70 miles down, but is the suggested average volume-change (*loc. cit* p. 1180), an explanation and a warning being added:—"As regards the estimated magnitude of this expansional effect, the amount of the voluminar expansion assumed is, to some extent, arbitrary. The upper part of the Magma may, indeed, enlarge or contract by some 10 per cent. of its volume in changing from solid to liquid and *vice versa*. The volume-change of the deeper parts is unknown, but if—as appears probable—there is vertical circulation of super-heated material, the volume-change may be considerable. The assumption of a mean change of 10 per cent. may, however, be somewhat excessive" (p. 1181).

In the book which Professor Lees is reviewing, a deeper basaltic substratum is considered and an average volume-change of 7 per cent. is assumed. This involves an allowance of five-twelfths for the average pressure effect; for, as pointed out in the early paper (referred to above) appearing in this Journal, and also in 'The Surface History of the Earth,' the experimentally determined volume-change of diabase from crystalline solid to liquid is 12 per cent. (not 10 per cent.).

I think it will be apparent from what I have stated that the two difficulties specially raised by Professor Lees are, in point of fact, non-existent. The calculation of volume-change of the substratum has been as fully considered as the available data permitted; but—and this is additional to what has appeared in my book—recent statements by high authorities on the subject of crustal shortening attending the revolutions and on the number of the revolutions would seem to permit of lower estimates of the depth of the substratum involved or of its average volume-change or of both.

I hope to revert to this subject at a later date.

April 6th, 1926.

XVIII. *Orthogonal Potentials.* *By* P. J. Daniell, *Sc.D.**

In this paper are introduced what we call orthogonal potentials as an aid in applying the minimum energy method to some simple problems in elasticity and hydrodynamics. The particular advantage gained is that we can apply the formulæ directly to any particular case by the substitution of numerical values which depend only on second and higher moments which are themselves calculable by simple quadratures.

In the first part of the paper we confine our attention to two-dimensional problems in which a function $f(x, y)$ is to be found satisfying Laplace's equation $\Delta f = 0$ within the area A and taking on given values $f(x, y) = a(x, y)$ on the boundary B of A. We assume that the boundary is so simple that the minimum energy method will lead, if properly used, to an approximate solution of the problem; so that we neglect the difficulties which would be raised by the mathematical purist.

A potential, $f(x, y)$, is a function possessing second-order derivatives and satisfying

$$\Delta f = \partial^2 f/\partial x^2 + \partial^2 f/\partial y^2 = 0$$

throughout the interior of A.

We define the *potential-product* of two potentials, f, g, as

$$[f \cdot g] = \int \left(\frac{\partial f}{\partial x}\frac{\partial g}{\partial x} + \frac{\partial f}{\partial y}\frac{\partial g}{\partial y} \right) d\mathrm{A} \div \mathrm{A},$$

integrating over the area A and dividing by the whole area A.

Two potentials, f, g, are said to be *orthogonal* if their potential-product is zero, *i. e.* if

$$[f \cdot g] = 0.$$

A set of potentials, $\phi_1, \phi_2, \ldots$, is said to be *normal* if

$$[\phi_i \cdot \phi_j] = 0, \quad i \neq j,$$
$$= 1, \quad i = j.$$

A set of potentials, $\phi_1, \phi_2, \ldots$, is said to be *complete* if there is no continuous potential ψ (other than a constant) such that for all values of i,

$$[\phi_i \cdot \psi] = 0.$$

In the same way as in the case of orthogonal sets of functions in the more usual sense, it is possible, given a complete set of linearly independent potentials, to form from

* Communicated by the Author.

them by linear combinations a complete and normal set of potentials.

In the first place, given any potential, g, we can normalize it by introducing a factor α, α being the reciprocal of the square-root of $[g \cdot g]$.

Let $g_1, g_2, \ldots$ be a complete set of potentials, and take

$$f_1 = \alpha_1 g_1, \quad f_2 = \alpha_2 (g_2 - f_1[g_2 \cdot f_1]),$$

$$f_3 = \alpha_3 (g_3 - f_1[g_3 \cdot f_1] - f_2[g_3 \cdot f_2]),$$

$$f_n = \alpha_n (g_n - f_1[g_n \cdot f_1] - f_2[g_n \cdot f_2] - \ldots - f_{n-1}[g_n \cdot f_{n-1}]),$$

where $\alpha_1, \alpha_2, \ldots \alpha_n, \ldots$ are the factors which normalize $f_1, f_2, \ldots f_n, \ldots$ It can readily be proved that f_2 is orthogonal to f_1, and that if $f_1, f_2, \ldots f_{n-1}$ are orthogonal to one another, f_n is orthogonal to all of them. Furthermore, since the f's now form a normal set,

$$\alpha_n^2([g_n \cdot g_n] - [f_1 \cdot g_n]^2 - \ldots - [f_{n-1} \cdot g_n]^2) = 1.$$

By the usual form of Green's theorem, if f and g are potentials,

$$\mathrm{A}[f \cdot g] = \int f \partial g / \partial n \, ds = \int g \partial f / \partial n \, ds,$$

integrating round the boundary B of A, when δn is an element of normal *outwards* from A.

Indeed, provided only that g be a potential,

$$\mathrm{A}[f \cdot g] = \int f \partial g / \partial n \, ds.$$

If f is a potential and $\phi_1, \phi_2, \ldots$ a normal set of potentials, let

$$c_n = [f \cdot \phi_n],$$

$$f_n = c_1 \phi_1 + c_2 \phi_2 + \ldots + c_n \phi_n.$$

Then

$$[(f - f_n) \cdot (f - f_n)] = [f \cdot f] - 2c_1[f \cdot f_1] - \ldots - 2c_n[f \cdot f_n] + c_1^2 + \ldots + c_n^2,$$

$$= [f \cdot f] - (c_1^2 + \ldots + c_n^2).$$

But, by definition, for any g, $[g \cdot g]$ is non-negative, so that

$$c_1^2 + c_2^2 + \ldots + c_n^2 \leq [f \cdot f].$$

It follows that

$$c_1^2 + c_2^2 + \ldots$$

is either a finite or a converging series, and hence that

$$g = c_1 \phi_1 + c_2 \phi_2 + \ldots$$

exists *. Furthermore

$$[(f - g) \cdot \phi_n] = [f \cdot \phi_n] - [g \cdot \phi_n] = c_n - c_n = 0.$$

* A proof is possible in the case of areas of a certain simplicity, but our present interest is in the applications.

Hence, if the set $\phi_1, \phi_2, \ldots$ is *complete* as well as normal,

$$c_1\phi_1 + c_1\phi_2 + \ldots$$

determines the true solution f, except for an additive constant. But on the boundary

$$f(x, y) = a(x, y)$$

is given, so that

$$c_n = [f \,.\, \phi_n] = \int f \partial\phi n/\partial n \, ds/\mathrm{A},$$
$$= \int a \partial\phi_n/\partial n \, ds/\mathrm{A}$$

is known, and the solution, f, is completely determined.

Also if $a(x, y)$ is known, not only on the boundary B but also throughout A, and possesses first derivatives,

$$c_n = \int\left(\frac{\partial a}{\partial x}\frac{\partial \phi_n}{\partial x} + \frac{\partial a}{\partial y}\frac{\partial \phi_n}{\partial y}\right) d\mathrm{A}/\mathrm{A}.$$

In particular if, as in the cases to be considered,

$$a = \tfrac{1}{2}(x^2 + y^2),$$
$$c_n = \int\left(x\frac{\partial \phi_n}{\partial x} + y\frac{\partial \phi_n}{\partial y}\right) d\mathrm{A}/\mathrm{A}.$$

In an actual case it will be necessary to choose a suitable set of potentials $g_1, g_2, \ldots$, and then to determine the corresponding normal set. After that the constants $c_1, c_2, \ldots$ will be evaluated, but it will be unnecessary to proceed beyond a certain stage, since the assumptions made in reducing the actual problem to a simple mathematical form will introduce errors of appreciable magnitude.

Polynomial Potentials.

We are given the area A, and we shall choose axes of coordinates passing through the centre of area and so as to be principal axes for second moments. That is to say, we shall have

$$\int x d\mathrm{A} = \int y d\mathrm{A} = \int xy d\mathrm{A} = 0.$$

Let k^2 be the square of the polar radius of gyration,

$$k^2 = \int (x^2 + y^2) d\mathrm{A}/\mathrm{A},$$
$$\lambda = \int (x^2 - y^2) d\mathrm{A}/\mathrm{A}k^2,$$

so that λ is a pure number between ± 1. For an ellipse of semi-axes a, b or a rectangle of sides $2a$, $2b$,

$$\lambda = (a^2 - b^2)/(a^2 + b^2).$$

It can be verified that

$$\phi_1 = x, \quad \phi_2 = y, \quad \phi_3 = (x^2 - y^2)/2k, \quad \phi_4 = xy/k$$

form, so far, a normal set.

Since they are each homogeneous, the constants c_1, c_2, etc., can easily be found. Indeed,

$$c_1 = c_2 = c_4 = 0,$$
$$c_3 = 2\int \phi_3 d\mathrm{A}/\mathrm{A} = \int (x^2 - y^2) d\mathrm{A}/\mathrm{A}k = \lambda k.$$

Hence

$$f_4 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$$
$$= \lambda(x^2 - y^2)/2.$$

This formula would be exact for an ellipse of semi-axes a, b.

For the cubic terms take

$$v_5 = \tfrac{1}{3}x^3 - xy^2, \quad v_6 = x^2y - \tfrac{1}{3}y^3,$$

and let

$$\int v_5 d\mathrm{A}/\mathrm{A} = k^2\beta_5, \quad \int v_6 d\mathrm{A}/\mathrm{A} = k^2\beta_6,$$
$$\int x(x^2 + y^2) d\mathrm{A}/\mathrm{A} = k^2\xi, \quad \int y(x^2 + y^2) d\mathrm{A}/\mathrm{A} = k^2\eta,$$
$$\int (x^2 + y^2)^2 d\mathrm{A}/\mathrm{A} = k^4\rho^2.$$

Then

$$[\phi_1 . v_5] = [\phi_2 . v_6] = \lambda k^2,$$
$$[\phi_2 . v_5] = -[\phi_1 . v_6] = 0,$$
$$[\phi_3 . v_5] = [\phi_4 . v_6] = k\xi,$$
$$[\phi_4 . v_5] = -[\phi_3 . v_6] = k\eta,$$
$$[v_5 . v_6] = 0, \quad [v_5 . v_5] = [v_6 . v_6] = k^4\rho^2.$$

Hence

$$\phi_5 = [\tfrac{1}{3}x^3 - xy^2 - \lambda k^2 x - \xi(x^2 - y^2)/2 + \eta xy]/k^2\rho',$$
$$\phi_6 = [x^2y - \tfrac{1}{3}y^3 - \lambda k^2 y - \eta(x^2 - y^2)/2 - \xi xy]/k^2\rho',$$

where

$$(\rho')^2 = \rho^2 - \lambda^2 - (\xi^2 + \eta^2)/k^2$$

Also

$$x\partial v_5/\partial x + y\partial v_5/\partial y = 3v_5, \text{ etc.}$$

Hence

$$c_5 = (3\beta_5 - \lambda\xi)/\rho',$$
$$c_6 = (3\beta_6 - \lambda\eta)/\rho',$$
$$f_6 - f_4 = c_5\phi_5 + c_6\phi_6$$
$$= (3\beta_5 - \lambda\xi)[\tfrac{1}{3}x^3 - xy^2 - \lambda k^2 x - \xi(x^2 - y^2)/2 + \eta xy]/\rho'^2 k^2$$
$$+ (3\beta_6 - \lambda\eta)[x^2y - \tfrac{1}{3}y^3 - \lambda k_2 y - \eta(x^2 - y^2)/2 - \xi xy]/\rho'^2 k^2.$$

The corresponding exact forms of the fourth degree are so

complicated that it is advisable to make some simplifying assumption. In practice, unless the cubic terms are very small—when, for example, there is practical symmetry about each of the two axes—the fourth-order terms will only give a small correction. In either case very little error is introduced by calculating the fourth-order terms as if the third-order constants were negligible. Hence we now take

$$\beta_5=\beta_6=\xi=\eta=0,$$
$$\phi_5=(x^3/3-xy^2-\lambda k^2x)/k^2\rho',$$
$$\phi_6=(x^2y-y^3/3-\lambda k^2y)/k^2\rho'.$$

Take

$$v_7=(x^4-6x^2y^2+y^4)/4, \quad v_8=x^3y-xy^3,$$

and let

$$\int v_7 dA/A=k^4\beta_7, \quad \int v_8 dA/A=0,$$
$$\int xy^3 dA=\int x^3y dA=0,$$
$$\int(x^4-y^4)dA/A=\lambda' k^4,$$
$$\int(x^2+y^2)^3 dA/A=\sigma^2k^6.$$

Then

$$\partial v_8/\partial x=3x^2y-y^3=-\partial v_7/\partial y,$$
$$\partial v_8/\partial y=x^3-3xy^2=+\partial v_7/\partial x,$$
$$[\phi_1\,.\,v_7]=[\phi_2\,.\,v_8]=[\phi_2\,.\,v_7]=-[\phi_1\,.\,v_8]=0,$$
$$[\phi_3\,.\,v_7]=[\phi_4\,.\,v_8]=\lambda' k^3,$$
$$[\phi_4\,.\,v_7]=-[\phi_3\,.\,v_8]=0,$$
$$[\phi_5\,.\,v_7]=[\phi_5\,.\,v_8]=[\phi_6\,.\,v_7]=-[\phi_5\,.\,v_8]=0,$$
$$[v_7\,.\,v_8]=0, \quad [v_7\,.\,v_7]=[v_8\,.\,v_8]=\sigma^2k^6.$$

Hence

$$\phi_7=[(x^4-6x^2y^2+y^4)/4-\lambda' k^2(x^2-y^2)/2]/k^3\sigma',$$
$$\phi_8=[x^3y-xy^3-\lambda' k^2xy]/k^3\sigma',$$

where

$$(\sigma')^2=\sigma^2-\lambda'^2.$$

Also

$$c_7=(4\beta_7-\lambda\lambda')k/\sigma', \quad c_8=0,$$
$$f_8-f_5=c_7\phi_7+c_8\phi_8$$
$$=(4\beta_7-\lambda\lambda')[(x^4-6x^2y^2+y^4)/4-\lambda' k^2(x^2-y^2)/2]/k^2\sigma'^2.$$

Application to Torsion *.

If θ is the twist, l the length of the rod, n the modulus of rigidity, the resultant couple Q is given by

$$Q=n\left(\frac{\theta I}{l}-\int\left(x\frac{\partial\psi}{\partial x}+y\frac{\partial\psi}{\partial y}\right)dA\right)$$

where $\Delta\psi=0$ throughout A and

$$\psi=\theta(x^2+y^2)/2l$$

on the boundary. Put $\psi=\theta\phi/l$ so that, on the boundary,

$$\phi=\tfrac{1}{2}(x^2+y^2).$$

Then ϕ is the solution obtained above, and

$$\begin{aligned}Q&=\frac{n\theta}{l}\left(I-\int\left(x\frac{\partial\phi}{\partial x}+y\frac{\partial\phi}{\partial y}\right)dA\right)\\&=\frac{n\theta}{l}\left(I-\Sigma_i c_i\int\left(x\frac{\partial\phi_i}{\partial y}+y\frac{\partial\phi_i}{\partial y}\right)dA\right)\\&=n\theta(A/l)(k^2-\Sigma_i c_i^2)=\kappa n\theta I/l.\end{aligned}$$

In general, if the area does not depart too far from the circular or elliptic, the terms in c_3, c_4 will be the most important, and c_7, c_8 are small terms in which we can make approximating assumptions without fear of great error. In view of Saint Venant's approximate formula (p. 177),

$$Q=n\theta A^4/40Il,$$

it is convenient to express κ in the form

$$\kappa=fA^4/40I^2=fA^2/40k^4,$$

so that

$$f=40\kappa(k^2/A)^2$$

and is a pure number not far from 1.

Substituting the values of the c's,

$$\begin{aligned}\kappa=1-\lambda^2-&[(3\beta_5-\lambda\xi)^2+(3\beta_6-\lambda\eta)^2]/k^2\rho'^2\\&-(4\beta_7-\lambda\lambda')^2/\sigma'^2\end{aligned}$$

to this order of approximation.

Illustrations.—Ellipse.

In this case, by symmetry, $\beta_5=\beta_6=\xi=\eta=0$,

$$\begin{aligned}Ak^4(4\beta_7-\lambda\lambda')&=\int(x^4-6x^2y^2+y^4)dA-\lambda\int(x^4-y^4)dA\\&=A[c_4(a^4+b^4)-6c_2a^2b^2-\lambda c_4(a^4+b^4)],\end{aligned}$$

where c_4, c_2 are the average values of x^4, x^2y^2 for a unit

* The references will be to Prescott, 'Applied Elasticity,' as here, p. 140.

circle. But for a circle

$$2c_4 - 6c_2 = \text{average of } r^4 \cos 4\theta = 0 ;$$

$$k^4(4\beta_7 - \lambda\lambda') = c_4[(a^4 + b^4 - 2a^2b^2) - \lambda(a^4 - b^4)]$$
$$= c_4(a^2 - b^2)[(a^2 - b^2) - \lambda(a^2 + b^2)] = 0.$$

Hence, as we knew beforehand, the third- and fourth-order terms disappear. Indeed, the second terms give an exact solution, and

$$\kappa = 1 - \left(\frac{a^2 - b^2}{a^2 + b^2}\right)^2 = \frac{4a^2b^2}{(a^2 + b^2)^2} = \frac{1}{4\pi^2}\frac{A^2}{k^4},$$
$$f = 40/4\pi^2 = 1{\cdot}01.$$

Rectangle.

In this case, again by symmetry,

$$\beta_5 = \beta_6 = \xi = \eta = 0,$$
$$\lambda = (a^2 - b^2)/(a^2 + b^2), \quad k^2 = (a^2 + b^2)/3,$$
$$k^4(4\beta_7 - \lambda\lambda') = \int(x^4 - 6x^2y^2 + y^4)dA/A - \lambda\int(x^4 - y^4)dA/A,$$
$$4\beta_7 - \lambda\lambda' = -12a^2b^2/5(a^2 + b^2)^2,$$
$$\lambda' = 9\lambda/5,$$
$$\sigma^2 = 27[(a^6 + b^6)/7 + a^2b^2(a^2 + b^2)/5]/(a^2 + b^2)^3,$$
$$= 27(3 + 2\lambda^2)/35,$$
$$\sigma'^2 = 27(15 - 11\lambda^2)/175,$$
$$\kappa = (1 - \lambda^2) - 112a^4b^4/3(15 - 11\lambda^2)(a^2 + b^2)^4,$$
$$f = \frac{10}{9}\left[1 - \frac{7}{3}\frac{1 - \lambda^2}{15 - 11\lambda^2}\right]$$
$$= 1 - \frac{5 - 7{\cdot}4\lambda^2}{27(3 - 2{\cdot}2\lambda^2)}.$$

For a square $a = b$, $\lambda = 0$, and

$$f = 1 - 5/81 = 0{\cdot}938,$$

while Prescott's result (from p. 153) is

$$f = 0{\cdot}937.$$

If $b = 2a$, $\lambda = -0{\cdot}6$,

$$f = 0{\cdot}961 \text{ (Prescott, } 0{\cdot}953).$$

If $b = 4a$, $\lambda = -0{\cdot}8824$,

$$f = 1{\cdot}022 \text{ (Prescott, } 0{\cdot}995).$$

The two values are identical when $b/a = \infty$, namely 10/9. However, it must be remembered that Prescott's method for

the rectangle could not be applied to any other shape; whereas our method is equally suitable for any compact area and is the result of applying a minimum energy method assuming a fourth-power function only.

Isosceles Triangle.

Take the x-axis to be the symmetric median of the triangle, $3h$ being the length of this median, and let the length of the perpendicular side be $2a$. In the case of an equilateral triangle,

$$a=\sqrt{3}h.$$

We shall neglect the fourth-order terms. Also on account of the symmetry about the x-axis,

$$\beta_6=\eta=0,$$
$$A=3ah, \quad k^2=(3h^2+a^2)/6,$$
$$\lambda=(3h^2-a^2)/(3h^2+a^2).$$

We observe that λ is zero for an equilateral triangle which agrees with the fact that for such an area the second momental ellipse reduces to a circle.

$$\beta_5=2h(h^2+a^2)/5(3h^2+a^2)=2k(2-\lambda)\sqrt{(1+\lambda)/15},$$
$$\xi=2h(3h^2-a^2)/(3h^2+a^2)=2k\lambda\sqrt{(1+\lambda)/5},$$
$$\rho^2=12(9h^4+2a^2h^2+a^4)/5(3h^2+a^2)^2=4(2+\lambda^2)/5,$$
$$\rho'^2=(40-9\lambda^2-4\lambda^3)/25,$$
$$3\beta_5-\lambda\xi=2k(2-\lambda-\lambda^2)\sqrt{(1+\lambda)/5},$$
$$\kappa=3(1-\lambda^2)\frac{8+\lambda^2}{40-9\lambda^2-4\lambda^3},$$

or, approximately, if λ^2 is small,

$$f=\frac{8}{9}\left(1+\frac{7\lambda^2}{20}+\frac{\lambda^3}{10}\right).$$

For an equilateral triangle λ is zero,

$$f=8/9=0\cdot889,$$

which corresponds to the value obtained by Prescott (p. 177). In fact, in this case, the potential is of the third degree, so that our approximation is exact.

For a right-angled isosceles triangle, $a=3h$,

$$\lambda=-1/2,$$
$$f=1-2/45=0\cdot96,$$

while if $h=a$ so that the semi-vertical angle of the triangle is arc tan 1/3,

$$f=0\cdot98.$$

Application to Viscous Flow.

If the pressure difference is p, the length of the tube l and the coefficient of viscosity η, then

$$p/l = \eta \Delta w$$

throughout A, while on the boundary

$$w = 0.$$

Put

$$w = p[\tfrac{1}{2}(x^2+y^2) - \phi]/2l\eta\ ;$$

then throughout A, $\Delta\phi = 0$ and on the boundary

$$\phi = (x^2+y^2)/2,$$

so that ϕ is the same function as that found in the case of torsion. The total rate of flow is

$$Q = \int w d\mathrm{A} = [p/2l\eta][\tfrac{1}{2}\mathrm{I} - \int \phi d\mathrm{A}]$$

$$= \frac{p}{2l\eta}(\tfrac{1}{2}\mathrm{I} - \Sigma_i c_i \int \phi_i d\mathrm{A}).$$

Now $c_1 = c_2 = 0$ and ϕ_3, ϕ_4 are homogeneous of the second degree, so that

$$c_3 = 2\int \phi_3 d\mathrm{A}/\mathrm{A}, \quad c_4 = 2\int \phi_4 d\mathrm{A}/\mathrm{A} = 0.$$

Then, as far as the second-order terms,

$$Q = p(\mathrm{I} - \mathrm{A}c_3^2)/4l\eta = p\mathrm{I}(1-\lambda^2)/4l\eta.$$

ϕ_5, ϕ_6 are not homogeneous, but differ from homogeneous expressions of the third order by linear terms whose integrals vanish, and quadratic terms with small integrals when the tube is of comparatively compact shape. Hence we may take, approximately,

$$c_5 = 3\int \phi_5 d\mathrm{A}/\mathrm{A},$$

and similar results for c_6 and the fourth-order terms. Hence we may take

$$Q = (p\mathrm{A}/4l\eta)[k^2(1-\lambda^2) - 2(c_5^2+c_6^2)/3 - (c_7^2+c_8^2)/2].$$

Indeed, if we only desire a rough approximation, we can again use Saint Venant's formula and obtain

$$Q = \frac{p\mathrm{A}^4}{160 l\eta \mathrm{I}}.$$

Three Dimensions.

There is not space in this paper to consider the application of the method to three-dimensional problems in general, but we can give a few indications of the development.

The body equations * are

$$m\,\partial\Delta/\partial x + n\nabla^2 u + \rho X = 0,$$

and two similar equations. At the surface the equations for a free body are

$$\lambda[(m-n)\Delta + 2n\partial u/\partial x] + \mu[n(\partial v/\partial x + \partial u/\partial y)] + \nu[n(\partial u/\partial z + \partial w/\partial x)] = 0,$$

together with two similar equations, where λ, μ, ν are the direction-cosines of the normal to the surface.

Let ϕ denote a vector displacement field (u, v, w) and let ϕ' denote the corresponding stress tensor (P_1, P_2, P_3, S_1, S_2, S_3),

$$P_1 = (m-n)\Delta + 2n\partial u/dx,$$
$$S_1 = n(\partial w/\partial y + \partial v/\partial z)$$

$(\phi')_n$ denotes the vector force obtained by combining ϕ' with the direction (λ, μ, ν), so that the x-component of $(\phi')_n$ is

$$\lambda P_1 + \mu S_3 + \nu S_2.$$

Moreover, $\psi \,.\, (\phi')_n$ is the scalar product of the vectors ψ and $(\phi')_n$.

Let $E(\phi \,.\, \phi)$ denote the elastic energy per unit volume due to the displacement $\phi = (u, v, w)$. Then *

$$2E(\phi \,.\, \phi) = P_1\alpha + P_2\beta + P_3\gamma + S_1 a + S_2 b + S_3 c = \phi' \,.\, \phi'',$$

where ϕ' is the above stress tensor corresponding to ϕ, while ϕ'' is the strain tensor $(\alpha, \beta, \gamma, a, b, c,)$,

$$\alpha = \partial u/\partial x, \quad a = \partial v/\partial z + \partial w/\partial y, \text{ etc.}$$

Similarly, we define

$$2E(\phi \,.\, \psi) = \phi' \,.\, \psi'' = \phi'' \,.\, \psi'$$

and

$$W(\phi \,.\, \psi) = 2\int E(\phi \,.\, \psi)\, dV/V,$$

integrated over the volume of the body.

An elastic field, ϕ, is a field which satisfies the body equations (for the given elastic constants) with no body forces.

Two elastic fields, ϕ, ψ, are said to be *orthogonal* if

$$W(\phi \,.\, \psi) = 2\int E(\phi \,.\, \psi)\, dV/V = 0.$$

* Prescott, p. 27.
† Prescott, p. 188.

We can proceed as before to consider *normal* and *complete* sets of elastic fields.

If ψ is an elastic field it can be proved by a form of Green's theorem, called Betti's theorem, that

$$\mathrm{VW}(\phi \cdot \psi) = \int \phi'' \cdot \psi' \, dV = \int_B \phi \cdot (\psi')_n dS,$$

where the last integral is taken over the bounding surface of the body.

Centrifugal Force.

Let us consider, in particular, the problem of an elastic body rotating uniformly about a fixed axis under no forces except the centrifugal force. Let the z-axis be taken on the axis of rotation and let r be the distance from this axis. Choose

$$u_0 = xr^2/8(m+n), \quad v_0 = yr^2/8(m+n), \quad w_0 = 0.$$

Then
$$P_1 = [(2m+n)x^2 + (2m-n)y^2]/4(m+n) = \pi_1,$$
$$P_2 = [(2m-n)x^2 + (2m+n)y^2]/4(m+n) = \pi_2,$$
$$P_3 = (m-n)(x^2+y^2)/2(m+n) = \pi_3,$$
$$S_1 = S_2 = 0, \quad S_3 = nxy/2(m+n) = \sigma.$$

Let ω be the angular velocity of rotation, U, V, W the actual displacements, and put

$$U = \rho\omega^2(u - u_0), \text{ etc.}$$

In this case $\phi = (u, v, w)$ is actually an "elastic field," that is, a field due to no body forces. On the surface

$$(\phi')_n = (\lambda\pi_1 + \mu\sigma, \quad \lambda\sigma + \mu\pi_2, \nu\pi_3),$$

so that $(\phi')_n$ is determinate on the surface.

If $\phi_1, \phi_2, \ldots$ is a complete normal set of elastic fields and if

$$c_r \int_B \phi_r \cdot (\phi')_n \, dS/V = \int_B \phi_r \cdot (\phi_0')_n \, dS/V,$$

the required solution is given by

$$\phi = c_1\phi_1 + c_2\phi_2 + \ldots$$

If the system is completely balanced without the addition of further forces and couples,

$$\int xz \, dV = \int yz \, dV = 0,$$

and we can choose the x and y axes so that

$$\int xy \, dV = 0.$$

In this case there will be six independent "fields" which are linear in x, y, z (corresponding to constant strain tensors).

Take

$$f_1=(0, z, y), \quad f_2=(z, 0, x), \quad f_3=(y, x, 0),$$
$$f_4=(x, y, z), \quad f_5=(x, -y, 0), \quad f_6=(x, y, -2z).$$

These fields will be orthogonal to one another and the first six normal fields will be

$$\phi_1=f_1/2\sqrt{n}, \quad \phi_2=\text{etc.},$$
$$\phi_4=f_4/\sqrt{(9m-3n)},$$
$$\phi_5=f_5/2\sqrt{n}, \quad \phi_6=f_6/2\sqrt{(3n)}.$$

Of independent fields of the second degree there will be fifteen, but we shall leave their determination to a later paper. The normal set obtained by proceeding to the third and higher degrees will be applicable not only to the problem of rotating bodies but to the general statical elastic problem in three dimensions.

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XIX. *Interatomic Distances in Crystals.*

By Prof. W. L. Bragg, *M.A.*, *F.R.S.**

1. In a paper in this Magazine, the author in 1920 [4] gave figures for the radii of atoms deduced from their arrangement in crystals. It was shown that in many cases the distance between neighbouring atoms in a crystal corresponded closely with the sum of the constants for the two atoms concerned, and it was proposed to use this empirical relationship as an aid to X-ray analysis.

Since this paper appeared, other investigators have treated the same problem in a much more fundamental way, and have used data which were not available at the time the original paper was published. The author is in agreement with their more satisfactory treatment of the problem, and has adopted their point of view. Since the figures of the 1920 paper have recently been quoted in several instances, it appears desirable to publish the present note.

2. The examination of a large number of crystal structures has provided a wealth of data on interatomic distances in

* Communicated by the Author.

solid bodies. Two ways in which these data may be employed are relevant to the present discussion.

On the one hand, the observed distances may be interpreted by expressions for the mutual potential energy of two atoms in close proximity. From these expressions the condition for the equilibrium of the forces between atom and atom in the crystal may be formulated. This is, of course, the most fundamental way of treating the problem, and must finally supersede other methods. The classical instance of its application is Born's treatment [5] of the alkaline halides and other simple salts. Recently Lennard-Jones [18] has published a most interesting series of papers in which he has linked up the forces between atom and atom in the inert gases, and the corresponding forces in simple crystalline structures composed of ions of similar electronic configuration to the inert gases.

On the other hand, we may make use of empirical relationships which have been found to hold with a very fair degree of accuracy for interatomic distances in crystals. The existence of these relationships is probably due to the rapid increase of the repulsive force between two ions as the distance between them diminishes *. This makes it possible, without taking account of the very complicated interaction of forces in a crystal of a complex type, to form an estimate of the distance between neighbouring atoms which is sufficiently accurate for the first stages in the analysis of the structure. Although the exact distance between two neighbouring atoms will depend on the way in which all the surrounding atoms are arranged, as well as on the particular pair under consideration, yet the distance remains approximately constant for a given pair from crystal to crystal. The empirical rules enable one to estimate the point at which the repulsive forces will be of the right order to balance the forces of attraction tending to compress the crystal structure.

This is the assumption which is made when "spheres of influence" are assigned to the ions, and when the atoms are regarded as being elastic bodies packed together and supported by their neighbours. Any given set of figures will only hold for a series of crystals in which there is the same type of chemical bond between the atoms, but this restriction also applies to any calculations based on expressions for mutual potential energy.

* For instance, the compressibilities of the alkaline halides indicate that the force would be doubled by a decrease in interatomic distance of 7 per cent., if the extrapolation can be carried so far.

In analysing a complex crystal, an estimate of the probable distance between any pair of neighbouring atoms is of the greatest assistance. The positions of the atoms in the crystal are determined by a number of parameters, and the difficulty of analysis increases with this number. Structures with two or three parameters can be attacked in a straightforward manner, all possible values of the parameters being considered and those discarded which do not conform to the observed intensities of X-ray diffraction. As the number of parameters increases, this process becomes so laborious that any method of shortening it is of value. Knowledge of the quantitative laws governing X-ray diffraction is rapidly increasing, and in the author's opinion a point has been reached where reliance may be placed on solutions of crystal structure containing a large number of parameters, when it can be shown that these solutions explain in a satisfactory manner the intensity of the observed reflexions. Many reflexions can be measured in order to check the results, so that there is no lack of equations which must be satisfied by the variable parameters. The difficulty of analysis is similar to that of solving a number of simultaneous equations, and this difficulty is greatly reduced if approximate values of the parameters can be obtained in a simple manner, or certain ranges of their values excluded from consideration as being highly improbable. Empirical rules based on crystals already analysed are of value for this purpose and may be used legitimately. It is not intended to suggest that a structure based on these can be regarded as satisfactorily solved. The final test of the solution must consist in a proof that the proposed atomic arrangement explains the X-ray data, and that no alternative arrangement will do so.

Any attempt to assign radii, or spherical domains, to the ions must be an unsatisfactory compromise, for one is not dealing with definite physical quantities. It must, of course, be recognized that analysis of the functions defining the forces between atoms, such as Lennard-Jones has carried out, supersedes the cruder conception of a certain space occupied by each atom to the exclusion of other atoms. At the same time, the importance of this latter conception in X-ray analysis must not be disregarded. It will probably be true for some time yet that the crystal structures which can be made to yield to X-ray analysis surpass in complexity those to which mathematical analysis can conveniently be applied. Quite approximate estimates of interatomic distance may be used as the first step towards

analysis, and it must be counted a fortunate result of the nature of atomic fields that the conception of atoms occupying a characteristic amount of space in the crystal structure to the exclusion of others gives results in a very fair agreement with observation. This conception can be immediately used, however complex the structure, whereas an application of known force-constants can hardly be made until the structure is at any rate approximately determined.

4. A list of atomic or ionic radii has, therefore, as its sole justification its convenience as a means of summarizing observed distances, and of making possible a first approximation to the relative positions of atoms in a structure which is under investigation. Limiting consideration in the first place to cases where the bonds are of the polar type, in the generally accepted meaning of the term, there are, broadly speaking, two sets of ionic radii which have been proposed. Both are based on the undoubted fact that interatomic distances are additive in many series of compounds. They differ in that the one set (proposed by the author in 1920, and Niggli [6] in 1921) assigned values of the radii to the cations which were larger than those of the other set (proposed by Wasastjerna [12] in 1923, and foreshadowed by Landé [1] in 1920) by a constant amount of about 0·7 Å. All the anions in the first set are correspondingly smaller by the same amount.

The second set correspond much more closely with the physical reality, in so far as such an arbitrary idea as that of ionic radius can correspond with reality. The author believes that they are preferable for this reason. Both sets give the same estimate of the point at which the repulsion between cation and anion sets in, but the second set also gives an estimate of the point at which the repulsion between anions sets in. Now in actual crystal structures it is often found that in certain directions anions are nearest neighbours. In these cases (where a non-polar bond between the atoms is absent) the author's figures give far too small an estimate of the distance between the anions, whereas Wasastjerna's figures correspond satisfactorily with the observed value.

Wasastjerna's figures were proposed with a clear recognition of their fictitious nature, and with a preliminary discussion of the atomic force-fields which determine interatomic distances. They are given below as ionic radii in Ångström units.

TABLE I.

O −− 1·32	F− 1·33	Na^+ 1·01	Mg^{++} 0·75
S −− 1·69	Cl− 1·72	K^+ 1·30	Ca^{++} 1·02
S −− ?	Br− 1·92	Rb^+ 1·50	Si^{++} 1·20
Te−− ?	I− 2·19	Cs^+ 1·75	Ba^{++} 1·40

This list may be extended to a number of other ions. NH_4^+ and Tl^+ replace Rb^+ with very small alteration in interatomic distance. Pb^{++} replaces in a similar manner Sr^{++}. Be^{++} and Al^{+++} are so small that interatomic distances are generally determined by the mutual repulsion of atoms surrounding them, rather than by repulsion between these metals and the neighbouring anions. In this sense the ions Be^{++} and Al^{+++} may be regarded as fitting into the spaces between the surrounding atoms. Fe^{++}, Co^{++}, Ni^{++}, Zn^{++} are nearly equivalent to Mg^{++}.

Though this set of figures does not apply to atoms united by non-polar bonds, it may be extended to more complex acid radicals such as CO_3^{--}, NO_3^-, ClO_4^-, SO_4^{--}, $SiO_4^{==}$. In every crystal that has so far been analysed, the oxygen atoms in these acid radicals are grouped in a symmetrical way, at the corners of an approximately equilateral triangle in CO_3^{--} and NO_3^-, and at the corners of an approximately regular tetrahedron in ClO_4^-, SO_4^{--}, $SiO_4^{==}$. The distances between oxygen atoms are as follows :—

CO_3^{--}, NO_3^-	2·25 Å. ($CaCO_3$, $NaNO_3$).
SO_4^{--}, ClO_4^-	2·45 Å. ($CaSO_4$, $BaSO_4$, $LiKSO_4$, $RbClO_4$).
$SiO_4^{==}$	2·55 Å.–2·7 Å. (Mg_2SiO_4).
	2·7 Å.–2·85 Å. ($Ca_3Al_2Si_3O_{12}$).

These distances between oxygen atoms show wide variations from group to group as might be expected. However, the distance between an oxygen atom of a group, and a neighbouring cation or anion, is given quite satisfactorily by the additive law. A model of the structure may be made by representing the oxygen atoms centred at the points given by the above dimensions, and having radii of about 1·35 Å.

The author * has modified the atomic radii which he originally proposed for purposes of analysis in the way suggested by Wasastjerna. It is very striking, in working

* W. L. Bragg, Address to the Franklin Institute, Sept. 1924; Solvay Conference (Chemistry) Brussels, April 1925; Royal Institution Discourse, May 1925.

out a new structure, to observe how closely the first approximation obtained by packing together an assemblage with the dimensions of the atomic domains, corresponds with the final structure attained by a careful consideration of the intensities of reflexion. One cannot help being convinced that the idea is useful, and gives a helpful conception of the reasons for the stability of the structure.

Small alterations in Wasastjerna's figures might perhaps be made in order to get a better general correspondence with observed distances, but their approximate nature makes this hardly worth doing.

A very large number of papers on atomic radii have been published, of which only a few are mentioned below. In 1920, Landé [6], in a paper on "The Sizes of Atoms," showed that the interatomic distances in the alkaline halides were approximately additive. Starting with the assumption that in lithium iodide the size of the structure is determined by the repulsions between the iodine atoms, he obtained a set of values for the apparent sizes of the monovalent ions with which Wasastjerna's values are in agreement. Fajans and Herzfeld [3] in 1920 pointed out that the additive law was approximate, and investigated types of fields of force which would explain the observed distances. A very careful review of the molecular volumes of the alkaline halides by Spangenberg [14] showed a regular deviation from an additive law of interatomic distance even in this simple series compounds. A paper by Grimm [8] gives a very complete summary of the relative dimensions of simple and complex ions, as shown by the comparison of isomorphous compounds. Davey [7] made a series of measurements of the alkaline halides, and showed how closely they obeyed an additive law. He proposed a set of atomic radii, based on assigning equal values to K^+ and Cl^-, Rb^+ and Br^-, etc. Everything would point, however, to a structure on a larger scale for the anion than for the corresponding cation. Wyckoff [13], in a paper "On the Hypothesis of Constant Atomic Radii," confirmed the application of the additive law to simple salts, while drawing attention to the many discrepancies which appear if it is applied to elements and compounds of all types. Starting from a different point, he obtained a set of figures corresponding closely to those published by the author. Pease [10] discussed the interatomic distances in diamond-type crystals, and showed that by themselves they formed a consistent series.

5. Wasastjerna, in his paper "On the Radii of Ions," quotes

instances where the set of figures he proposes explains structures in which anions are nearest neighbours. One of these is the structure of lithium iodide, which has already been mentioned in referring to Landé's paper. Another is the structure of $Mg(OH)_2$ and $Mn(OH)_2$, analysed by Aminoff. The author's figures, in assigning a small size to the oxygen, leave a large amount of space to be occupied by the hydrogen atom. The structure should rather be regarded, according to Wasastjerna, as a set of ions $(OH)^-$ in a near approach to hexagonal close-packing, with much smaller positive ions in the interstices.

We may add some other instances. The crystals CdI_2[11], ZrS_2, $ZrSe_2$[17], have a structure similar to that of $Mg(OH)_2$, the anions being much larger than the cations. In SnI_4[15][16], the iodine atoms are nearly in close-packing. Dickinson remarks that the distance between iodine atoms is about 4·21 Å, as it is in CdI_2, this value being much greater than that deduced from the author's atomic radii. Wasastjerna's figures give estimates for the distances between anions in all these cases which are in agreement with observation.

G. B. Brown and the author[19] have recently drawn attention to some crystals where the distance between oxygen ions is nearly constant throughout the structure, and has an average value of 2·7 Å. In BeO, Al_2O_3, $BeAl_2O_4$, the oxygen atoms are in a close approximation to hexagonal close-packing, and the dimensions of the assemblage are very nearly the same in each case. To illustrate this, we may imagine a rectangular cell containing sixteen points of the hexagonal close-packed assemblage, at a distance apart of 2·7 Å., to be referred to orthohexagonal axes. This is done in order to facilitate the comparison with chrysoberyl, $BeAl_2O_4$, which has orthorhombic symmetry. In the table, the dimensions of this cell are compared with cells containing sixteen oxygen atoms for BeO, Al_2O_3, and $BeAl_2O_4$.

Table II.

	a.	*b*.	*c*.
Close-packed assemblage	4·41	9·35	5·40
BeO	4·38	9·32	5·38
Al_2O_3	4·32	9·50	5·48
$BeAl_2O_4$	4·42	9·39	5·47

A paper by G. Menzer[21] has recently appeared on the

structure of garnet, $Ca_3Al_2Si_3O_{12}$. In this paper Menzer quotes the author's figures for atomic radii and compares them with the interatomic distances in the structure he suggests, finding in most cases a fair agreement. The author would prefer, however, an interpretation of the structure on rather different lines, laying stress on the distance between neighbouring oxygen atoms. Menzer's figures are as follows :—

	Observed.	Sum of "Atomic Radii."
Si–O.....	1·71 Å.	1·82 Å.
Ca–O	2·31 Å.	2·35 Å.
Al–O	1·95 Å.	2·00 Å.

If the author has interpreted Menzer's structure correctly, each oxygen atom has, as nearest neighbours, a calcium atom and eight other oxygen atoms. The distance Ca—O is significant, as the calcium ion is too large to be packed between oxygen ions. In the rest of the structure the Si and Al atoms fit into the spaces between the oxygen atoms, so that we would expect the latter to be at an average distance of about 2·7 Å. apart. The actual distances between an oxygen atom and its eight oxygen neighbours are, in ngström units, 2·68, 2·68, 2·79, 2·79, 2·85, 2·85, 2·70, 2·84. This both supports the estimate of 2·7 Å. as the distance at which the repulsion between the two ions O^{--} assumes a large value, and is a striking confirmation of the accuracy of Menzer's analysis.

6. The author's paper in 1920 has been criticized as an attempt to prove that atoms under all circumstance occupied an absolute rigid spherical domain, though this interpretation was guarded against by the statement "This additive law is only intended to be regarded as a working approximation, an aid to the analysis of complex structures." Cases which did not correspond with the additive law were quoted, and it was also pointed out that the "atomic radii" did not correspond with the relative dimensions of the atomic structures. The correspondence was deliberately sacrificed in order to obtain a set of figures which held for both polar and non-polar bonds. The analyses of structures which have since been made have shown that this cannot be realized.

In examining crystal structures, however, it is difficult to avoid the impression that the representation of the repulsive

forces by a simple inverse power of the interatomic distance is as much a compromise as the conception of atomic domains. The actual law of force is probably much more complex. The repulsion may be taking place between those parts of the atomic structure which approximate most closely, so that a mathematical expression for the force which tended to an infinitely high value for a finite distance between atomic centres might be closer to the truth and hold over a wider range than an inverse power of the distance. The close approximation to an additive law may receive its explanation along these lines.

The discussion of the nature of the repulsive force is beyond the scope of the present note, which is an attempt to show that the conception of atomic domains can render very useful service in crystal analysis, when due care is used in its application and its limitations are recognized.

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XX. *The Compton Scattering and the Structure of Radiation.* *By* T. L. Eckersley, *M.A.* *

COMPTON †, in discussing the scattering of X-rays by free electrons, has evolved a theory which frankly discards the laws of electromagnetism in favour of purely quantum considerations. In justification, he points out the inability of the classical theory to account for the change in wave-length in the scattered radiation, which experiments have shown undoubtedly occurs when very hard γ- or X-rays are used as the exciting source.

In making this statement he must have been unaware of an investigation by Sir J. J. Thomson ‡, who showed that ions or electrons are set in motion in the direction of propagation of electric waves, so that the scattering is effected by electrons which are moving along with the wave. To a fixed observer the scattered radiation will therefore appear of longer wave-length than that of the exciting source, in agreement with experimental results.

The formula evolved by Sir J. J. Thomson is :

$$c^2-(c-v)^2 = \frac{e^2c^2\mathrm{H}^2}{m^2p^2} \quad \text{or} \quad \frac{e^2\mathrm{H}^2\lambda^2}{4\pi^2m^2},$$

where c is the velocity of light, v the average drift produced in the direction of propagation, λ the wave-length, e and m the charge and mass of the electron respectively, and H the magnetic force in the wave-front.

A numerical examination of this formula shows that for wave-length of 0·1 Å. the change of wave-length is infinitesimal unless enormous values of H are involved.

In the following investigation the classical methods are employed, and Sir J. J. Thomson's analysis is extended to take account of the relativity variation of mass.

In accordance with quantum ideas, however, the steady state is calculated neglecting the reaction due to re-radiation or scattering, this process being assumed to take place in a sudden transition from one quantum state to another. The steady state is thus unaffected by re-radiation.

In the classical theory the change of wave-length is a function of the intensity of the incident radiation. If in accordance with the experimental evidence the scattered

* Communicated by the Author.

† Phys. Review, xxi. p. 483 (1923).

‡ J. J. Thomson, Phil. Mag. ser. 6, vol. iv. p. 253 (August 1902).

frequency is only a function of the incident frequency, there must be a restriction on the intensity of the incident radiation. The assumption that this is in quanta is insufficient to determine this relation, for this only fixes the total energy $h\nu$ in the quantum, and not the intensity of E, which determines the change of frequency.

In the present theory the relation is provided by quantizing the orbit of the scattering electrons, which is found to be periodic. Such a process is perhaps rather outside the scope of the usual quantum theory, which to my mind merely exhibits the four-dimensional (dynamic) structure of the atom; but the theory must stand by the test of results, and these appear to be in accordance with the experimental evidence.

To accept the process outlined here seems to me to be more logical than to discard, with Compton, the whole structure of the electromagnetic laws, which are undoubtedly valid in the lower frequency ranges.

The method which uses the classical theory to calculate the steady states, and only involves the quantum theory to restrict the possible states (or calculate the arbitrary constants), has the merit of retaining the classical theory as far as possible, and is logically self-consistent if we consider the classical theory as exactly applicable to all periodic or quasi-periodic states of motion, and the quantum theory as a guide to define the possible steady states and the probability of transfer of one state to another.

Before entering into mathematical details of the problem, it may be worth while to attempt to give a mental picture of the physical processes which result in the production of a drift of electrons in the direction of propagation, according to the classical theory. Thus an isolated electron in the field of a plane electromagnetic wave will, under the influence of the electric force, in the first place, execute a vibration to and fro along the lines of electric force, *i. e.* at right angles to the direction of propagation of the waves. But in doing so it cuts across the lines of magnetic force H in the wave-front, and is given a resultant forward impulse. It will be found that the mean force is zero when averaged over a large number of periods, so that there is no resultant acceleration, and the average velocity given in the first impulse remains unaltered.

This average velocity v is a function of the frequency and intensity of the incident radiation, and $\frac{v}{c}$ measures the change of frequency of the scattered radiation.

To state the problem explicitly, let us suppose a plane wave :

$$\mathrm{E} = \mathrm{E}_0 \sin p(t - x/c), \quad t > x/c, \quad \mathrm{E} = 0 \text{ for } t < x/c,$$
$$\mathrm{H} = \mathrm{H}_0 \sin p(t - x/c), \quad \text{,,} \quad \mathrm{H} = 0 \quad \text{,,}$$

moving from left to right along the x axis to meet a stationary electron at $x=0$, $y=0$, and $z=0$.

Let the electric force be in the z direction and the magnetic force in the y direction.

The general equations for the movement of the electron are :

$$-m_0 \left\{ \frac{d^2 x_\mu}{ds^2} + \{\alpha\beta, \mu\} \frac{dx_\alpha}{ds} \frac{dx_\beta}{ds} \right\} = \mathrm{F}_\nu^\mu \mathrm{J}^\nu, \quad . \quad * \quad (1.1)$$

where J^ν is the current vector

$$\rho \frac{dx}{dt}, \quad \rho \frac{dy}{dt}, \quad \rho \frac{dz}{dt}, \quad \rho c.$$

F_μ is the tensor

$$\left.\begin{array}{cccc} 0 & -\gamma & \beta & \mathrm{X} \\ \gamma & 0 & -\alpha & \mathrm{Y} \\ -\beta & \alpha & 0 & \mathrm{Z} \\ +\mathrm{X} & -\mathrm{Y} & -\mathrm{Z} & 0 \end{array}\right\}, \quad . \quad . \quad . \quad . \quad (1.2)$$

assuming Galilean coordinates.

Also

$$\left.\begin{array}{l} \gamma = \alpha = 0, \\ \mathrm{X} = \mathrm{Y} = 0, \\ \{\alpha\beta, \mu\} = 0. \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1.3)$$

We get the equation :

$$\left.\begin{array}{l} m_0 \dfrac{d^2 z}{ds^2} = \rho \mathrm{Z} - \rho\beta \dfrac{dx}{dt}, \\ m_0 \dfrac{d^2 x}{ds^2} = \rho\beta \dfrac{dz}{dt}, \\ m_0 \dfrac{d^2 ct}{ds^2} = \mathrm{Z}\rho v_2. \end{array}\right\} \quad . \quad . \quad . \quad . \quad (1.4)$$

* Eddington, 'Mathematical Theory of Relativity,' pp. 118, 181.

For our purpose, since β is a function of t, $\beta=\beta_0 e^{ip\left(t-\frac{x}{2}\right)}$, it is best to modify the equation as follows:

$$m_0 \frac{d^2x}{ds^2} = m_0 \frac{d}{ds}\left(\frac{dt}{ds}\cdot\frac{dx}{dt}\right). \quad . \quad . \quad . \quad . \quad (1.5)$$

Now $m_0 \frac{dt}{ds} = m$, the value of the mass of the moving electron referred to fixed axes.

$$\frac{d^2x}{ds^2} = \frac{d\mathrm{M}_x}{ds}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.6)$$

where M_x is the X component of the momentum of the electron, and

$$\frac{d\mathrm{M}_x}{ds} = \frac{dt}{ds}\cdot\frac{d\mathrm{M}_x}{dt}; \quad . \quad . \quad . \quad . \quad (1.7)$$

so that

$$\left.\begin{aligned} \frac{d\mathrm{M}_x}{dt} &= \rho\frac{ds}{dt}\cdot\mathrm{Z}-\rho\frac{ds}{dt}\cdot\frac{dx}{dt}\cdot\beta, \\ \frac{d\mathrm{M}_z}{dt} &= \rho\frac{ds}{dt}\cdot\frac{dz}{dt}\cdot\beta, \\ \frac{dmc}{dt} &= \mathrm{Z}\rho\frac{ds}{dt}\cdot\frac{dz}{dt}. \end{aligned}\right\} \quad . \quad . \quad . \quad (1.8)$$

Now $\rho\frac{ds}{dt}$ = invariant charge e, so that

$$\left.\begin{aligned} \frac{d\mathrm{M}_x}{dt} &= e\mathrm{Z}-e\beta v_x, \\ \frac{d\mathrm{M}_x}{dt} &= e\beta v_z, \\ \frac{dme}{dt} &= \mathrm{Z}ev_z, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1.9)$$

or, expressing everything in terms of the four vectors M_x, M_y, M_z, mc,

$$\left.\begin{aligned} \frac{d\mathrm{M}_x}{dt} &= e\mathrm{Z}-\frac{e\beta}{m}\cdot\mathrm{M}_x, \\ \frac{d\mathrm{M}_x}{dt} &= \frac{e\beta}{m}\mathrm{M}_z, \\ m\frac{dme}{dt} &= \mathrm{Z}ev_z. \end{aligned}\right\} \quad . \quad . \quad . \quad (1.10)$$

If we use units for which E and H are of the same

dimensions (as a matter of convenience), the equations are obviously :

$$\left.\begin{aligned} \frac{dM_z}{dt} &= eZ-\frac{e\beta}{mc}M_x, \\ \frac{dM_x}{dt} &= \frac{e\beta}{mc}M_x, \\ m\frac{dmc}{dt} &= ZeM_z, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1.11)$$

the last being the activity equation.

§ 2. We have

$$M_z = \frac{mc}{e\beta}\cdot\frac{dM_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

and

$$\frac{dM_z}{dt} = \frac{d}{dt}\frac{mc}{e\beta}\frac{dM_x}{dt}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.2)$$

Substituting in (1·9) for $\frac{dM_z}{dt}$, we get

$$\frac{d}{dt}\frac{mc}{e\beta}\frac{dM_x}{dt} = eZ-\frac{c\beta}{me}M_x. \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

Multiplying both sides by $\frac{mc}{e\beta}\frac{dM_x}{dt}$, and denoting this quantity by U, we get

$$U\frac{dU}{dt} = \frac{Zmc}{\beta}\frac{dM_x}{dt}-M_x\frac{dM_x}{dt}, \quad . \quad . \quad (2.4)$$

$$\frac{1}{2}\frac{dU^2}{dt} = \frac{Zme}{\beta}\frac{dM_x}{dt}-\frac{1}{2}\frac{dM_x}{dt}, \quad . \quad . \quad (2.5)$$

or

$$\frac{1}{2}\frac{d}{dt}(U^2+M_x{}^2) = mc\frac{dM_x}{dt}, \text{ since } Z=\beta. \quad . \quad . \quad (2.6)$$

If we could consider m to be constant, we could get an approximate integral by integrating through with respect to t, but we can proceed more accurately as follows :—

The quantity

$$M_x,\ M_y,\ M_z,\ -mc \quad . \quad . \quad . \quad . \quad . \quad (2.7)$$

is a four-vector, and the invariant

$$M_x{}^2+M_y{}^2+M_z{}^2-m^2c^2 = -m^2.c^2 \quad . \quad . \quad . \quad (2.8)$$

in the special case of relativity. In this case, $M_y=0$,

$$M_x{}^2+M_z{}^2-m^2c^2 = -m^2.c^2, \quad . \quad . \quad . \quad . \quad (2.9)$$

or differentiating,

$$\frac{d}{dt}(\mathrm{M}_x^2+\mathrm{M}_z^2)=\frac{d}{dt}m^2c^2 \quad . \quad . \quad . \quad . \quad (2.10)$$

Now the energy equation derived from 1 and 2 gives

$$\frac{d}{dt}\left(\frac{\mathrm{M}_x^2+\mathrm{M}_z^2}{2}\right)=e\mathrm{Z}\mathrm{M}_x. \quad . \quad . \quad . \quad . \quad (2.11)$$

Now

$$m\frac{d\mathrm{M}_x}{dt}=\frac{dm\mathrm{M}_x}{dt}-\mathrm{M}_x\frac{dm}{dt} \quad . \quad (2.12)$$

and

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{m}\frac{d}{dt}\frac{m^2}{2}=\frac{\mathrm{M}_x}{m}\frac{d}{dt}(\mathrm{M}_x^2+\mathrm{M}_z^2), \quad (2.13)$$

$$=\frac{\mathrm{M}_x}{m}\frac{e\mathrm{Z}}{c^2}\mathrm{M}_z. \quad . \quad . \quad (2.14)$$

Substituting for M_z from (2.1),

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{m}\cdot\frac{e\mathrm{Z}}{c^2}\frac{mc}{c\beta}\frac{d\mathrm{M}_x}{dt}=\frac{\mathrm{M}_x}{c}\frac{d\mathrm{M}_x}{dt}; \quad (2.15)$$

so

$$cm\frac{d\mathrm{M}_x}{dt}=\frac{d}{dt}\left(cm\mathrm{M}_x-\frac{\mathrm{M}_x^2}{2}\right). \quad . \quad . \quad . \quad . \quad (2.16)$$

We have therefore expressed the right-hand side of (*a*) as a perfect differential with respect to t, which we may write now as

$$\tfrac{1}{2}\mathrm{U}^2=cm\mathrm{M}_x-\mathrm{M}_x^2+c, \quad . \quad . \quad . \quad . \quad (2.17)$$

where c is a constant.

A result which is useful is contained in equation (2.15), *i. e.* :

$$\mathrm{M}_x\frac{dm}{dt}=\frac{\mathrm{M}_x}{c}\frac{d\mathrm{M}_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad (2.18)$$

or

$$m=m_0+\frac{\mathrm{M}_x}{c}. \quad . \quad . \quad . \quad . \quad . \quad (2.20)$$

It is to be remarked that U in our equation (2.4),

$$\mathrm{U}=\frac{mc}{e\beta}\frac{d\mathrm{M}_x}{dt}=\mathrm{M}_z, \quad . \quad . \quad . \quad . \quad (2.21)$$

so that 2·4 may be re-written :

$$\tfrac{1}{2}\mathrm{M}_z^2+\mathrm{M}_x^2=cm\mathrm{M}_x+c. \quad . \quad . \quad . \quad (2.22)$$

Now M_x and M_z are zero together (initially), so that the arbitrary constant c must be zero.

We have

$$\frac{1}{2}\left(\frac{mc}{e\beta}\cdot\frac{d\mathrm{M}_x}{dt}\right)^2 = cm\mathrm{M}_x - \mathrm{M}_x^2 \quad . \quad . \quad . \quad . \quad (2.23)$$

or

$$\left(\frac{d\mathrm{M}_x}{dt}\right)^2 = \frac{2e^2\beta^2}{c^2}\left\{\frac{c\mathrm{M}_x}{m} - \frac{\mathrm{M}_x^2}{m^2}\right\} \quad . \quad . \quad (2.24)$$

Now

$$\frac{\mathrm{M}_x}{m} = v_x = \frac{\mathrm{M}_x}{m_0 + \dfrac{\mathrm{M}_x}{c}};$$

so that

$$\mathrm{M}_x = \frac{m_0 v_x}{(1-v_{x/c})} \quad \text{and} \quad m = \frac{m_0}{1-v_{x/c}} \quad . \quad . \quad . \quad (2.25)$$

We therefore get

$$\frac{d}{dt}\frac{m_0 v_x}{1-v_{x/c}} = \frac{\sqrt{2}e\beta}{c}\{cv_x - v_x^2\}^{1/2}, \quad (2.26)$$

$$\frac{1}{\{cv_x - v_x^2\}^{1/2}}\frac{d}{dt}\frac{m_0 v_x}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{c} \quad . \quad . \quad . \quad . \quad (2.27)$$

Now

$$\beta = \beta_0 e^{ip(t-x/c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.28)$$

and

$$\frac{d\beta}{dt} = \beta_0 e^{ip(t-x/c)} ip(1-v_{x/c})$$

since x is a function of t; . (2.29)

so that

$$\frac{1}{(v_{x/c})^{\frac{1}{2}}(1-v_{x/c})^{\frac{1}{2}}}\frac{d}{dt}\frac{v_{x/c}}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{cip(1-v_{x/c})}\frac{d\beta}{dt}, \quad (2.30)$$

or

$$\frac{(1-v_{x/c})^{\frac{3}{2}}}{(v_{x/c})^{\frac{1}{2}}}\frac{d}{dt}\frac{v_{x/c}}{(1-v_{x/c})} = \frac{\sqrt{2}e\beta}{m_0 cip}\cdot\frac{d\beta}{dt}; \quad . \quad . \quad (2.31)$$

and integrating,

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} = \frac{e\beta}{\sqrt{2}m_0 cip}\beta \quad . \quad . \quad (2.32)$$

Taking real parts,

$$\left.\begin{aligned}\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} &= \frac{e\beta}{\sqrt{2}m_0 cp}\cdot\sin\left(p(t-x/c)\right),\\ \left(\frac{v_{x/c}}{1-v_{x/c}}\right) &= \frac{e^2\beta^2}{2m_0^2c^2p^2}\sin^2 p(t-x/c).\end{aligned}\right\} \quad . \quad . \quad (2.33)$$

§(3) In this process we have made no mention of the type of wave-train involved. In any case we must suppose the electromagnetic disturbance to be zero until $t=0$ (at $x=0$).

The subsequent history of the wave-train, *i. e.* whether finite or extending to infinity, can only be conjectured.

If it is to be considered as a quantum of radiation, no doubt it is finite. The actual circumstances of the motion of the electron depend to a certain extent upon our choice of the type of wave-train, in particular upon whether the wave-front is a surface of discontinuity or not. At the outset let us take the simplest case, and suppose that the disturbance at $x=0$ is zero for negative values of $t-x/c$ and $\mathrm{R}.\beta_0 e^{ip(t-x/c)}$ for positive values of $t-x/c$.

Sommerfeld has shown that in this case the integral

$$\beta = \frac{\mathrm{R}}{2\pi}\beta_0 \int_{-\infty}^{+\infty} \frac{e^{ip(t-x/c)}}{(p-p_1)}\,dp \quad . \quad . \quad . \quad . \quad (3.1)$$

represents the complete disturbance if the integral is taken along the real axis, except in the neighbourhood of $p_2 p_1$, this point being encircled by a semicircle in the 4th quadrant. With this form of wave-train, Z and β are continuous at the wave-front, although $\dfrac{\partial\beta}{\partial x}$ and $\dfrac{\partial \mathrm{Z}}{\partial x}$ are not.

The continuity is associated with the fact that the Fourier integral is convergent at $t=x/c$.

The equation (2.32) still holds, even if we use this form, for

$$\beta = \frac{\mathrm{R}}{2\pi}\beta_0 \int_{-\infty}^{+\infty} \frac{e^{ip(t-x/c)}}{p-p_1}\,dp \quad . \quad . \quad . \quad . \quad . \quad (3.2)$$

and

$$\frac{d\beta}{dt} = \frac{\mathrm{R}}{2\pi}\beta_0(1 \quad v_{x/c}) \int \frac{ip\,dp\,e^{ip(t-x/c)}}{p-p_1}, \quad t-\frac{x}{c}\neq 0, \quad (3.3)$$

and $$= (1-v_{x/c})\frac{\mathrm{R}}{2\pi}\beta ip, \quad t-\frac{x}{c}\neq 0,$$

so long as

$$t-\frac{x}{c}\neq 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

As before,

$$\frac{v_{x/c}}{1-v_{x/c}} = \frac{e^2\beta^2}{2m_0{}^2c^2p^2}\sin^2(p)(t-x/c). \quad . \quad . \quad (3.5)$$

The more general case where Z and β are discontinuous at the wave-front can be formed by the integral :

$$\beta = \frac{\mathrm{R}}{2\pi}\beta_0 \int \frac{e^{i\phi}\,e^{ip(t-x/c)}\,p\,dp}{p-p_1}, \quad . \quad . \quad . \quad . \quad (3.6)$$

which is not convergent at $t-x/c=0$.

This quantity is zero if $t-x/c<0$, and is equal to

$$-\mathrm{R}\beta_0 i e^{i\phi} e^{ip(t-x/c)},$$

i. e., $\beta_0 \sin p(t-x/c+\phi)$,

when $t>x/c$.

Equation (3.5) is now modified by the addition of a constant:

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right)^{\frac{1}{2}} = \frac{e\beta_0}{\sqrt{2mcp}} \cdot \sin p(t-x/c+\phi) - \mathrm{C}, \quad . \quad (3.8)$$

and the constant C must equal $\sin\phi$, so that $v_x=0$ when $t=0$, as required.

Thus

$$\left(\frac{v_{x/c}}{1-v_{x/c}}\right) = \frac{e^2\beta_0^2}{2m_0^2c^2p^2} \{\sin(p(t-x/c)+\phi) - \sin\phi\}^2 \quad (3.9)$$

when the wave-front is discontinuous.

Reverting to our former expression, we can get the complete integral of the motion; *i. e.* the relation between x and t is as follows:—

If we put

$$p(t-x/c) = y, \quad . \quad . \quad . \quad . \quad . \quad (3.10)$$

then

$$\frac{dy}{dt} = p(1-v_{x/c})$$

and

$$\frac{v_{x/c}}{1-v_{x/c}} = \frac{e^2\beta_0^2}{2m_0^2c^2p^2}\sin^2 y = \zeta^2 \sin^2 y, \text{ say}, \quad . \quad (3.11)$$

or

$$pv_{x/c} = \zeta^2 \sin^2 y \frac{dy}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.12)$$

$$\frac{p}{c}\frac{dx}{dt} = \frac{\zeta^2}{2}\frac{d}{dt}\left(y-\frac{\sin 2y}{2}\right); \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.13)$$

and integrating,

$$\frac{px}{c} = \frac{\zeta^2}{2}\left(y-\frac{\sin 2y}{2}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.14)$$

$$\frac{x}{c} = \frac{\zeta^2}{2c}\left(t-\frac{x}{c}\right) - \frac{\zeta^2}{4p}\sin 2p\left(t-\frac{x}{c}\right). \quad . \quad (3.15)$$

No constant of integration is needed, since the condition $x=0$ when $t=0$ is satisfied identically by this relation. We thus have the required relation between x and t.

The corresponding values of v_z and Z may be obtained from (3), *i. e.*:

$$M_z = \frac{me}{e\beta}\frac{dM_x}{dt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.16)$$

$$= \frac{me}{e\beta}\frac{\sqrt{2}e\beta}{c}\{cv_x - v_x^2\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (3.17)$$

or

$$v_z = \sqrt{2}c\left(\frac{v_x}{c}\right)^{\frac{1}{2}}\left\{1-\frac{v_x}{c}\right\}^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (3.18)$$

$$v_z = \sqrt{2}(1-v_{x/c})\frac{(v_{x/c})^{\frac{1}{2}}}{(1-v_{x/c})^{\frac{1}{2}}}. \quad . \quad . \quad . \quad . \quad . \quad (3.19)$$

Thus

$$v_z = c(1-v_{x/c})\frac{e\beta_0}{m_0cp}\cdot\sin(p)(t-x/c)$$

$$= \frac{e\beta_0}{m_0p^2}\sin p(t-x/c)\frac{d}{dt}(t-x/c) \quad . \quad . \quad . \quad (3.20)$$

and

$$z = -\frac{e\beta_0}{m_0p^2}\{\cos p(t-x/c)-1\}$$

$$= -c\frac{\zeta}{p}\sqrt{2}\{\cos p(t-x/c)-1\}, \quad . \quad . \quad . \quad (3.21)$$

since $z=0$ when $t=0$.

§ (4) This forms the conclusion of the calculation of the steady state on the classical theory.

It will be observed that on this basis there is a definite drift of the electron with an average velocity $\frac{1}{4}\frac{e^2\beta_0^2}{m_0^2p^2c^2}$ ($v_{x/c}$ small) in the direction of propagation.

Combined with the periodic v_z motion this gives a scattered wave of a frequency which differs from that of the existing source by the amount $\delta\nu$, where $\frac{\delta\nu}{\nu}=\frac{v_x}{c}(1-\cos\theta)$, the scattering angle θ being the angle made with the positive normal to the wave-front.

In respect of the factor $1-\cos\theta$, the result agrees with that determined experimentally by Compton. The value, however, is a function of the intensity β of the incoming wave. There should therefore be no fixed value of the change of frequency unless there is a restriction on the value of β, occasioned, for instance, by the quantum structure of the incident radiation.

It might be thought sufficient at first sight to postulate the energy of the incident radiation as $h\nu$, where ν is the

frequency; but this determines only the total energy, and not the value of β, which determines the energy per unit volume. The procedure which naturally suggests itself is to treat the momentum M_z—which is periodic—according to the rules of the quantum theory, *i. e.* to suppose that the periodic motion of the electron is one of the specially determined steady quantum states.

We should then put

$$\oint M_z\,dz = nh,$$

and the process is more natural in that $\oint M_z\,dz$ expressed as a function of z turns out to be exactly an inverse periodic function, associated with which is the modulus of periodicity obtained by the integration round the two branch points of M_z.

Thus

$$\oint M_z\,dz = \oint \frac{mc}{e\beta}\cdot\frac{dM_z}{dt}\,dz \quad . \quad . \quad . \quad . \quad . \quad (4.1)$$

$$= \oint \frac{mc}{e\beta}\,\frac{\sqrt{2}e\beta}{c}(cv_x)^{\frac{1}{2}}(1-v_{x/c})^{\frac{1}{2}}. \quad . \quad (4.2)$$

Now

$$m = \frac{m_0}{1-v_{x/c}} \quad \text{by} \quad (2.25),$$

$$\oint M_z\,dz = \oint \frac{m_0\sqrt{2}c(v_{x/c})^{\frac{1}{2}}}{(1-v_{x/c})^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad (4.3)$$

$$= \oint \frac{e\beta}{pc}\cdot\sin\big(p(t-x/c)\big)\,dz. \quad . \quad . \quad (4.4)$$

Now, by (3.21),

$$\cos p(t-x/c) = \frac{zp}{c\zeta\sqrt{2}} + 1 \qquad = z', \text{ say}, \quad . \quad . \quad . \quad (4.5)$$

$$\sin p(t-x/c) = \sqrt{1-z'^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.6)$$

$$dz = c\zeta\sqrt{2}\,dz',$$

$$\oint M_z\,dz = \oint \frac{m_0 c\zeta\sqrt{2}}{p}\sqrt{1-z'^2}\,dz'c\zeta\sqrt{2} \quad (4.7)$$

$$= \frac{2m_0c^2\zeta^2}{p}\oint\sqrt{1-z'^2}\,dz$$

$$= \frac{2m_0c^2\zeta^2\pi}{p} = n_1h, \quad . \quad . \quad . \quad . \quad (4.8)$$

$$\zeta^2 = \frac{n_1h\nu}{m_0c^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.9)$$

for $n=1$, *i. e.* the 1-quantum state

$$\zeta^2 = \frac{h\nu}{m_0 c^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.10)$$

A guarantee of the general reasonableness of our choice in the method of quantizing the orbit of the electron is contained in the following relation :—

The total kinetic energy of the electron can be expressed, in accordance with the relativity theory, in the form :

$$(m-m_0)c^2 = \mathrm{KE}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.11)$$

Now

$$m = m_0 \frac{1}{1-v_{x/c}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.12)$$

$$\therefore \quad \mathrm{KE} = m_0 c^2 \left(\frac{v_{x/c}}{1-v_{x/c}}\right) \quad . \quad . \quad . \quad . \quad . \quad (4.13)$$

$$= m_0 c^2 \zeta^2 \sin^2 y$$

$$\mathrm{KE}_{\max.} = h\nu.$$

Now the energy equation gives

$$c^2 m \frac{dm}{dt} = m v_z \mathrm{Z} e, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.14)$$

$$c^2 \frac{dm}{dt} = v_z \mathrm{Z} e, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4.15)$$

$$\frac{d\mathrm{KE}}{dt} = \mathrm{Z} e \frac{dz}{dt}$$

or $$\frac{d\mathrm{T}+\mathrm{W}}{dt} = 0 \text{ and } \mathrm{T}+\mathrm{W} = h\nu, \quad . \quad (4.16)$$

where $$\mathrm{T} = \mathrm{KE}+\mathrm{W} = -\int \mathrm{Z} e \frac{dz}{dt}\, dt, \quad . \quad . \quad . \quad . \quad (4.17)$$

which is identically satisfied on using the expressions for Z and $\frac{dz}{dt}$ we have found in eq. (3·21)

The orbital energy is $h\nu$. This is in accordance with the ordinary notion of the quantum theory, since the initial state of the electron was one of zero energy level, and $h\nu$ is here given as the difference in energy level of the zero and 1-quantum state.

§ (5) This solution just obtained I would term "The Selected Semi-Classical Solution," to distinguish it from Compton's purely quantum solution. It corresponds exactly

to the solutions of the orbital motions of electrons under central forces in the atom.

I call it "selected," as quantum considerations are used in fixing the amplitude of the motions; it is semi-classical because in the equations of motion no account is taken of re-radiation or scattering, which, according to quantum principles, must be considered to be a separate process involving a change from one quantum state to another: this change, involving re-radiation, may be considered to take place when the train of waves has passed over the electron. We are therefore led to consider a second quantum state, and in accordance with the idea presented here, it should, if possible, be one which satisfies the field equations, the passage from the first to the second state being, of course, accompanied by a scattered radiation. The procedure which is perhaps least open to criticism from the quantum point of view, and for which there is strong experimental evidence, is to assume that, at least formally, this final state is the one calculated by Compton. The conservation of energy and momentum are used to calculate the path and velocity of the electron and the direction, intensity, and frequency of the scattered quantum, which is supposed to be a directed quantity.

This process is consistent on the average with the field equations.

The equations which fix this state are:

$$\left.\begin{aligned} \frac{h\nu}{c} &= \frac{h\nu_x'}{c} + \mathrm{M}_x, \\ 0 &= h\nu_\rho' - \mathrm{M}_\rho, \\ \nu_x'^2 + \nu_\rho'^2 &= \nu'^2. \end{aligned}\right\} \text{Momentum Equations,} \quad . \quad (5.1)$$

$$h\nu - h\nu' = (m - m_0)c^2, \quad \text{Energy Equation,} \quad . \quad . \quad (5.2)$$

$$\mathrm{M}_x^2 + \mathrm{M}_y^2 = (m^2 - m_0^2)c^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.3)$$

These equations give rise to the following frequency relation:

$$\frac{\delta\nu}{\nu} = \frac{\chi^2(1-\cos\theta')}{(1-\chi^2\cos\theta')}, \text{ where } \chi^2 = \frac{\dfrac{h\nu}{m_0c^2}}{1+\dfrac{h\nu}{m_0c^2}}, \quad . \quad . \quad (5{\cdot}4)$$

which is approximately

$$\frac{\delta\nu}{\nu} = \frac{h\nu}{m_0c^2}(1-\cos\theta'), \quad . \quad . \quad . \quad . \quad . \quad (5.5)$$

Correspondence.

This method exhibits the change of frequency on scattering as a purely quantum process, involving the idea of frequency as a determinant of the energy according to the relation $W = h\nu$; but it is the purpose of this paper to exhibit this change of frequency as a Doppler effect, in order to bridge over the gap between the Compton theory on one side and the classical theory on the other side, which undoubtedly applies to long-wave phenomena, and to use the idea of selected statical states for this purpose.

In this manner the solution (1) may be considered as a detailed expression of an intermediate state in the Compton analysis, introduced so as to bring this more in line with the usual methods of quantum analysis and to help to bridge over the gap just referred to.

In order to bring in the classical idea of Doppler effect, the following method may be used:—As we have seen, the process of re-radiation must occur in the jump from the first to the second quantum state. Since there is no re-radiation during the passage of the train of waves over the electron, the velocity of drift occasioned does not determine the Doppler change of frequency of the scattered radiation; but this latter must be determined by velocity after the change. By a suitable choice of the conditions at the end of the train we can continue the solution without discontinuity, so as to give an x velocity from which the Doppler effect corresponding to the Compton effect may be deduced.

Thus the x velocity determined from solution (1) is:

$$\frac{v_x}{c} = \frac{\frac{h\nu}{m_0c^2}\sin^2 p\left(t-\frac{x}{c}\right)}{\left\{1+\frac{h\nu}{m_0c^2}\sin^2 p\left(t+\frac{x}{c}\right)\right\}}. \quad . \quad . \quad . \quad (5.6)$$

If the train is chosen to end when

$$\sin p\left(t-\frac{x}{c}\right) = 1, \quad . \quad . \quad . \quad . \quad (5.7)$$

the value of $\frac{v_x}{c}$ will be

$$\frac{v_x}{c} = \frac{\frac{h\nu}{m_0c^2}}{1+\frac{h\nu}{m_0c^2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5.8)$$

and the corresponding Doppler effect will be

$$\frac{\delta\nu}{\nu} = \frac{v_x}{c}(1-\cos\theta) \doteq \frac{h\nu}{m_0c^2}(1-\cos\theta), \quad . \quad . \quad (5.9)$$

which corresponds with the Compton change of frequency.

Or we may arrive at the Doppler effect idea as follows:—

In developing the relation (5.5) from the equations (5.1), (5.2), (5.3) according to Compton's method, we get the relation

$$\mathrm{M}_x = \frac{h\nu}{c}(1-\cos\theta) \text{ approx.}, \quad . \quad . \quad (5.10)$$

or

$$\frac{v_x}{c} = \frac{h\nu}{mc^2}(1-\cos\theta),$$

and the corresponding Doppler effect would be

$$\frac{v_x}{c} = \frac{h\nu}{mc^2}(1-\cos\theta), \quad . \quad . \quad . \quad . \quad (5.11)$$

which is the relation already obtained.

Thus the change of frequency on scattering may either be considered as an effect due to the energy removed from the incident wave by the recoil electron, *i.e.* as a purely quantum energy change, or as a Doppler effect associated with the velocity v_x of recoil.

These two aspects enable one to pass over from the quantum aspect as developed by Compton to the classical aspect, which follows as a result of the application of the ordinary field laws, by the process of building up a statistical state from the individual quantum process, the relative probability of emission in various directions being determined by the field equations. The details of such a process must be left to a future paper.

The results obtained by the method of this paper are formally just the same as those obtained by Compton ; but the method outlined here seems to bring relation between the field equation and the quantum processes into a clearer light, and to pave the way to the understanding of the relation between the individual quantum processes on the one hand and the electromagnetic state as calculated from the field laws which apply on the longer waves on the other. The exhibiting of the quantum process as a selected classical solution, and the identification of the quantum and Doppler aspect of the change of frequency, ensures that a proper

choice of the statistical aggregate of quantum processes must conform to the ordinary field equations.

It should be noted that the Einstein conception of a quantum of radiation having a definite direction of travel in space is used throughout, and it seems to me that this is a logical necessity if quantum and relativity notions are to be reconciled.

For suppose the quantum were a spherical type wave, such as, for instance, is radiated from a source at 0 vibrating in a vertical direction, if the frequency were ν, the corresponding energy would be $h\nu$.

Now refer this system to a set of axes moving relatively to source with the velocity v: the various parts of the spherically-radiated quantum will have different frequencies, and the relation $W = h\nu$ will no longer have any meaning.

I have been guided throughout in fixing the quantum rules by the consideration that any quantity which can be defined in the classical theory—for instance, $\delta\nu/\nu = v/c$—should not clash with the quantum definition of $\delta\nu$, *i. e.* the same quantity. In this manner we have been led to a *definite* value of the change of frequency in scattering which has been observed.

It must be admitted, of course, that the work has been carried out with half an eye on the expected result; but the real value lies in the fact that the quantum conditions must be introduced, and these are naturally and inevitably introduced through the only really periodic quantity v_x. In using this we find the orbited energy to be in accordance with the known quantum principles.

We can picture the process outlined here as the arrival of a quantum $h\nu$ of radiation at the stationary electron, an absorption of this energy by the electron, and a consequent transference of this to the 1-quantum state with energy $h\nu$ (fixing the amplitude of oscillation M_z); finally, a transition from the 1-quantum state to the 2-quantum state, with an emission of scattered radiation with frequency and energy determined by the difference of energy level in the 1 and 2 states, *i. e.*,

$$h\nu' = h\nu - \frac{mv_x^2}{2} = W_1 - W_2,$$

each steady state being rigidly defined by the classical theory (of course neglecting the effect of re-radiation). It is then found that the change in frequency on scattering may either be regarded as a change of energy content of the radiation, or as a Doppler effect associated with the recoil velocity v_x, at least to the first approximation.

§ 6. The further consequences of this theory have a bearing on the structure of radiation.

This is rather to be expected, as this example illustrates perhaps the simplest case of interaction between the quantum and the electron.

The quantity ζ^2 has two interpretations. From the quantum point of view it is the ratio of the quantum of energy $h\nu$ to the potential energy of the electron m_0c^2. From the classical point of view it involves β^2, the energy density reckoned in the ordinary manner, thus :

$$\zeta^2 = \frac{h\nu}{m_0c^2} = \frac{e^2\beta^2}{m_0{}^2p^2c^2} \text{ (energy/vol.} = \beta^2 \text{ in our units)},$$

so that the energy density in the incident radiation is determined by the relation :

$$\beta^2 = \frac{m_0p^2/h\nu}{e^2} = \frac{4\pi^2m_0h\nu^3}{e^2} \quad . \quad . \quad . \quad . \quad . \quad (6.1)$$

Now we know the total energy in the incident radiation, i. e. $h\nu$; so that if β^2 is supposed to be uniformly distributed in space, the ratio $\frac{h\nu}{\beta^2} = \frac{e^2}{4\pi^2\nu^2m_0}$ should be the volume in which the quantum is contained, and in calculating this we should get an insight into the structure of radiation.

Now the quantity $\frac{e^2}{m_0c^2}$ has the dimensions of a length. In the usual electromagnetic theory it expresses the linear dimensions of the electron, according to the relation :

$$m_0 = \frac{e^2}{6\pi ac^2}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

$$\therefore \text{ Vol.} = \frac{e^2}{4\pi^2\nu^2\frac{e^2}{6\pi ac^2}} = \frac{3ac^2}{2\pi\lambda^2}, \quad . \quad . \quad . \quad . \quad (6.3)$$

or

$$\text{Vol.} = \frac{3a\lambda^2}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6.4)$$

where "a" is the radius of the electron.

Also we may put it in the form :

$$\text{Vol.} = \frac{4\pi a^3}{3}\frac{1}{2}\left(\frac{3}{2}\frac{\lambda}{2\pi a}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad (6.5)$$

so that the volume tends to that of an electron when $\lambda = \sqrt{2}\frac{2\pi a}{3}$; *i. e.*, the quantum apparently shrinks to electronic dimensions when the wave-length is of the order of the electronic radius.

A quantum no doubt consists of a finite train of oscillations. We may perhaps be allowed to consider the electron as remaining in the 1-quantum state during the time that this quantum train passes over the electron. Now by combining classical principles with Einstein's probability coefficients—*i. e.* $A_{1\to 2}$, $B_{2\to 1}$—E. A. Milne* has arrived at a formula which expresses the mean duration of a given quantum state. It is

$$\tau = \frac{c}{4\pi^2 a \nu^2}, \quad \ldots\ldots \quad (6.6)$$

an expression which, as has been pointed out, does not involve h and is therefore independent of the atomic structure, and should be applicable to the type of electronic vibration envisaged in this case.

In the present analysis exactly the same result can be obtained by assuming that on the average the re-radiation is what it would have been on the classical theory ; thus if τ is the average duration of the quantum state 1, $\frac{h\nu}{\tau}$ will be equal to the rate of radiation calculated on the classical lines. Thus

$$\frac{h\nu}{\tau} = \frac{1}{2}\frac{e^2}{6\pi}\frac{\Gamma^2}{c^3}, \quad \ldots\ldots \quad (6.7)$$

where Γ is the acceleration.

$$\Gamma = \frac{dv_z}{dt} = \frac{d}{dt}\frac{e\beta}{mp}\sin pt \text{ approx.}$$

$$= \frac{e\beta}{m}\cos pt. \quad \ldots\ldots \quad (6.8)$$

The mean rate of radiation of energy is therefore

$$\frac{1}{2}\frac{e^2p^2}{6\pi c^3}\left(\frac{e\beta}{mp}\right)^2,$$

and is independent of p.

* Monthly Notices R. A. S. p. 743, No. 8, June 1925.

$$\frac{h\nu}{\tau} = \frac{1}{2}\frac{e^2p^2}{6\pi c}\left(\frac{\beta e}{m_0 pc}\right)^2 = \frac{e^2p^2h\nu}{6\pi m_0 c^3}, \quad . \quad . \quad . \quad (6.9)$$

so that

$$\frac{1}{\tau} = \frac{e^2p^2}{6\pi m_0 c^3};$$

and since $m_0 = \frac{e^2}{6\pi a c^2}$,

$$\frac{1}{\tau} = \frac{4\pi^2\nu^2 a}{c} \text{ as before.} \quad . \quad . \quad . \quad (6.10)$$

But if we are to retain the same mental picture of the process as before, $c\tau$ must represent the length of a train of oscillations.

One curious consequence of this formula is the following:—

The number of oscillations in the train is $\nu\tau$, or $\frac{c}{4\pi^2 a\nu} = \frac{\lambda}{4\pi^2 a}$. The number of oscillations in a train tends to unity as $\lambda \to 4\pi^2 a$. This is in agreement with the fact that the quantum appears to shrink up to the size of an electron for this frequency. The quantum appears to lose its periodic nature at these high frequencies. What the meaning of $h\nu$ in the formula $W = h\nu$ is, very obscure! This result is perhaps only apparent and due to some approximation introduced into the last stage of the calculation, and is only true if $c\tau$ represents the actual length of the train of oscillations.

On this basis, the length of the train of oscillations is $c\tau$. We may now express the volume V in the form:

$$V = \frac{3ac^2}{2\pi\nu^2} = \frac{6a^2c^2}{4\pi^2\nu^2 a} = 6a^2c\tau. \quad . \quad . \quad . \quad (6.11)$$

From this point of view, the quantum appears to be contained within a cylinder or tube of radius $\sqrt{\frac{6a}{\pi}}$, or practically the electronic radius and length of $c\tau$. It is perhaps as well to note that this volume is not a fixed quantity; it seems to adjust itself to the radius of the particle acted upon by the quantum. For instance, if the electrified particle had been a proton, the equivalent value of "a" in formula would have been proportionally smaller, and the quantum would have to adjust itself to this smaller radius. These results inevitably suggest the tube of force attached to the electron or proton, the quantum being a disturbance propagated along this tube, as a state of distortion say.

The tube ends in its appropriate electron or proton, and its approximate diameter is correctly given if some latitude is allowed in fixing the structure of the electron or proton.

The motion of the tube must be fixed by the electromagnetic laws. It is well known, for instance, that the second set of circuital equations can be deduced from purely kinematic considerations of the movement of discrete tubes of force, if the magnetic force is interpreted as the velocity of the tube at right angles to itself.

The whole would form a very compelling picture, were it not that the interference effects are still wholly unexplained, and that the nature of the jump from one steady state to another is also physically difficult to picture.

If we take the view that it is the function of theory to provide an accurate mathematical description of the physical facts, the relativity quantum theory outlined here is singularly adequate—not that it is complete, since the framing of the quantum rules has certainly not been achieved yet.

A theory must pass a very strict test nowadays; it must not only be accurate, it must also be a convenient and powerful instrument of thought. It is a commonplace reflexion, for instance, that certain problems are much more easily solved in terms of certain coordinates than others, and that they may take on an aspect of artificial complexity if inconvenient coordinates are chosen. I have been struck throughout the foregoing analysis with the ease with which the solution unfolded itself; and although it would be foolish to take this as a guarantee of correctness, it certainly seems to indicate that it is a simple mode of expression of the realities involved in one of the simplest of quantum processes.

It will be seen that this scheme really differs very little from Compton's theory. The quantum of energy as portrayed by this theory is very similar to the material particle envisaged by Compton in his theory (for frequencies comparable with $\frac{m_0 c^2}{h}$), the contraction in volume being a striking example of this similarity. Compton's theory short-circuits the analytical details of this by using the principles of conservation of energy and momentum which are, of course, implicit in the present classical quantum theory. The present method may be perhaps looked upon as strengthening the assumption upon which Compton's theory is based—*i. e.*, that the quantum acts as a particle which exchanges its energy (in accordance with the ordinary laws of momentum and energy exchange) in a collision.

It is perhaps significant, in view of recent speculations concerning the transformation of matter into radiation (for

example, at intensely high temperatures in the interior of stars), that at these frequencies, *i. e.* of the order of $\frac{m_0c^2}{h}$, the distinction between the material element, *i. e.* electrons and protons, and the quantum of radiation seems to disappear, for the energy and volume are of the same order; and if we accept the approximate formula for the number of oscillations in a quantum, a relation which, however, seems to me of very doubtful validity, the quantum loses its periodic structure at these frequencies, and there is but little left to distinguish it from a proton or electron, say.

It is hoped that this paper may pave the way to a fuller understanding of the relation between the quantum and classical theories of radiation.

Perhaps too much stress should not be laid on the physical picture of the volume of a quantum as portrayed here; but if we are to retain our present ideas of time and space as extended by Einstein, we must regard this quantity at least as dimensionally a volume.

XXI. *Note on the Molecular Association of Benzoic Acid in Benzene.* *By* J. A. Wilcken, *B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne* *.

THE question as to the connexion between dielectric and other physical and chemical properties of matter, which has an important bearing on problems of cable insulation, has led to the investigation into the molecular nature of solutions, and as a type, benzoic acid in benzene has been examined.

Auwers † and his co-workers, and Beckmann ‡ have dealt with a large number of solutions of this class, but whereas the former attributes the abnormal behaviour (freezing-point depression) to mutual influence of solute and solvent, the latter inclines to the view that complex molecules are formed. Turner § leaves the question open.

This part of the work had been temporarily discontinued, but Prof. Partington's and Mr. Rule's valuable contribution to the subject in the May issue of this Journal suggested that the preliminary results here given might be of some interest.

* Communicated by the Author.

† *Zeitschr. Physikal. Chemie*, xii. pp. 689–722 (1893); *ibid.* xxx. pp. 300–340 (1899).

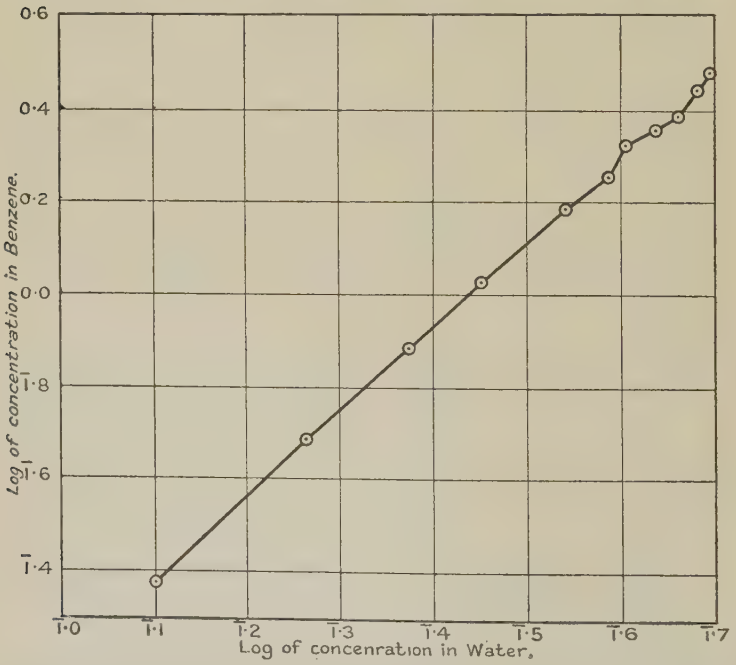
‡ *Ibid.* xxii. pp. 609–618 (1897).

§ 'Molecular Association' (Longmans).

Freezing-point determinations carried out with an ordinary Beckmann apparatus gave data too irregular to warrant any conclusive inference, although they seemed to point to a molecular weight swinging between $2\frac{1}{2}$ and $1\frac{1}{2}$ times the normal value.

A series of graded solutions was then prepared, of concentrations varying from 0·040 grm. to 0·564 grm. benzoic acid to 100 grms. benzene, and with these solutions the partition coefficients between pure (conductivity) water and benzene were determined, the titrations being carried out with a standardized baryta solution (ind. phenol-phthalein). The separating funnel was kept carefully at 6°·0 C.

The diagram below shows the relation between the log. of



the concentration in benzene and the log. of the corresponding concentration in water. It is seen that the slope of the line deviates appreciably from unity, indicating that the matter is not so simple as the formation of double molecules; the scale of abscissæ is twice that of the ordinates. Might not the process of association pass through a metastable and a labile state, somewhat similar to those of the crystallization of solutions, as found by Miers and Isaac* ?

* Journ. Chem. Soc. lxxxix. pp. 413–454 (1906).

XXII. *Further Studies on the Deformation of Tungsten Single Crystals.* *By* F. S. Goucher. (Communication from the Staff of the Research Laboratories of the General Electric Co., Wembley.) *

[Plates II.–V.]

Summary.

The crystals studied are the large crystals formed in recrystallized hard-drawn pure tungsten wires such as were used in the previous experiments, and in addition Pintsch single crystal wires which can be similarly deformed at lower temperatures.

Measurements on the rate of flow of the pure tungsten crystals under constant load at both 2000° K. and 1000° K. show an internal hardening which increases rapidly in the early stages of deformation and which tends to become proportional to the increase of stress in the later stages; this stage occupies the major portion of the time required for the fracture of such crystals. The hardening is greater at the lower temperature, and there is evidence that the rate of deformation is an important factor in the hardening process. This hardening may be removed by annealing at 2500° K. for 2 minutes.

An X-ray study of these crystals at all stages of their deformation reveals distortions—crystallographic in nature—which increase progressively with the degree of deformation. Annealing these crystals produces no apparent alteration of this distortion. Evidence is obtained that the stress is important in the determination of the degree of distortion. Fractured crystals show the distortion in a very marked degree.

A comparison of the resolving power of crystals deformed at 1000° K. in the hard and in the annealed states shows no measurable difference, whereas Pintsch wires similarly deformed at room temperature show an impaired resolving power which improves on annealing; this is not accompanied by any change in mean reflecting angle exceeding 0·05 per cent.

A microscopic examination of these crystals before and after annealing confirms the persistence of the crystal distortion but shows a pronounced difference in the etching effect which can only be explained by a greater differential rate of etching in the case of the unannealed crystals.

The experiments support the view that hardening is due to residual elastic strains produced by the deformation process rather than the mere fact of crystal break up.

(1) *Introduction.*

A systematic study of the strength of tungsten single crystals taking into account the relation between the

* Communicated by the Director.

rate of deformation on the one hand and the load, temperature, and crystal orientation on the other, has already been described*. The measurements were made by taking the time required to fracture fine tungsten wires composed of comparatively large crystals, many of which occupied locally the complete volume of the wire. When such wires were subjected to a constant load at any given temperature, deformation occurred in certain of these large crystals depending on their orientation, and one eventually fractured with the formation of a wedge-shaped structure symmetrically inclined to the stress. This structure was explained by a process of successive small slips parallel to two sets of crystal planes, and the time of fracture was considered as an inverse measure of the mean rate of flow along such planes. No attempt was made, however, to measure any variations in the rate of flow which might occur during the deformation process.

A subsequent investigation † associated the deformation with slip on definite crystallographic planes and in definite crystallographic directions—the (112) planes and the [111] directions—but revealed marked distortions, also of a crystallographic nature. These distortions appeared as bendings of the crystal planes about an axis at right angles to the direction of flow, and were of such a magnitude as to be inconsistent with the preservation of continuity of the crystal lattice as there appeared to be no marked alteration of the lattice parameters. It seemed probable that the hardening effect of deformation was in some way connected with these distortions.

The present experiments were initiated with the object of studying the variations of rate of flow throughout the deformation process as a measure of variations in slip resistance, and at the same time to study the distortions produced by the deformation both from the point of view of the break up of the crystal, and of any possible variations in the lattice parameter, in the hope of throwing further light on the cause of hardening due to deformation.

Some progress in this direction has been made by the study of single crystals of other metals. The facts of crystal hardening independent of changes of orientation, of the crystallographic nature of distortion, and of crystal

* Phil. Mag. xlviii. p. 229 (Aug. 1924).
† Phil. Mag. xlviii. p. 800 (Nov. 1924).

break up, have now been established. Some workers associate the cause of hardening with very small residual elastic strains as a logical consequence of the distortions, whereas others associate it with the boundary conditions between broken up crystal fragments. The difficulty has been the lack of direct X-ray evidence for the existence of the lattice strains or of experiments directly associating break up with the production of hardness or its removal. Recently van Arkel * has shown that broadened diffuse lines which become sharp on annealing may be obtained with hard-drawn fine wires of certain metals such as tungsten and platinum, whereas very soft metals like lead and tin do not show the effect. He ascribes the broadening to a distortion of the crystal lattice, but the fact that it might equally well have been produced by very small crystal fragments—as he himself has pointed out—makes the evidence inconclusive.

Our experiments have now reached a stage where they are of interest in this connexion, and the following account is therefore given.

(2) *Experimental.*

The test wires were prepared by annealing hard-drawn pure tungsten wires 0·2 mm. in diameter and 10 cm. in length to a temperature of 3100° K. for a period of 2 to 3 minutes, as in the case of the previous experiments. Owing to intercrystalline brittleness below 900° K. these wires could not be used for deformation at lower temperatures, and in cases where this was required Pintsch single crystal wires were used. Pintsch wires contain about 2 per cent. of thorium oxide, and a description of their preparation may be found elsewhere †.

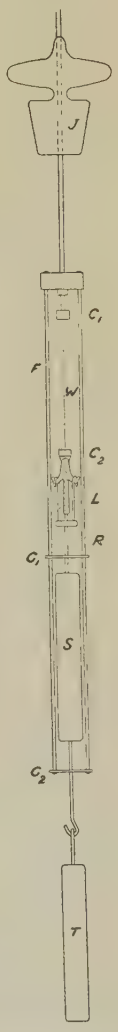
The methods employed for the heat treatment and deformation of these test wires were essentially the same as those used previously, the wires being heated electrically in a vacuum and the tension being applied by means of a tungsten and steel buoy floated in mercury.

One or two modifications of the old testing apparatus were required to facilitate the removal of the test wire from the vacuum apparatus at different stages of deformation for the purpose of measuring the degree of deformation of the

* A. E. van Arkel, Physica, v. p. 208 (1925).
† Bottger Z. Electrochemie, xxiii. p. 121 (1917).

individual crystals. The modified form is shown diagrammatically in fig. 1. The ground glass joint J supports a wire frame F carrying two guides G which limit the movement of the tungsten and steel buoy T S. The test wire is attached to a clamp C_1 fixed to the ground joint J and to a clamp C_2, which may be linked to the top of the buoy by means of two sets of hooks as shown ; it may be connected or disconnected at will by floating the buoy and turning the ground joint J while in position in the vacuum apparatus. A loose sleeve L attached to the clamp C_2 serves to keep the test wire in line with the connecting rod R_1 of the buoy. The clamp C_1 is insulated from the metal frame F, and is electrically connected to a wire passing through the ground joint J ; the other electrical connexion is made through the mercury used in floating the buoy.

Fig. 1.



The degree of deformation of the individual crystals in the test wires was measured in terms of the local reduction in diameter of the crystal. This was done by optical projection, the test wire being magnified about 40 times. The whole testing device was removed from the glass vacuum apparatus with the buoy disconnected. It was then mounted vertically in the projection apparatus in such a manner that the test wire could be rotated about its axis, and moved vertically with respect to the optical system. The deformed crystals could be photographed or measurements could be made directly by focussing on a ground glass screen.

Measurements of the extension of the test wire as a whole could be made directly through the glass of the vacuum apparatus by means of a cathetometer.

The methods of preparing sections of these crystals for purposes of X-ray and microscopic examination were the same as those described previously, with the exception that copper plating was substituted for the hard glass mounting in cases where it was necessary to retain the hardening effect of the deformation ; since it was found that the temperature required for mounting the test wires in hard glass was sufficient to remove some of the hardness. Polished sections of the deformed crystals were prepared and the

copper dissolved off. These were then etched according to the same standard formula in all cases, viz., 1 minute in boiling hydrogen peroxide and 45 seconds in alkaline potassium ferricyanide.

The X-ray study was made with the same spectrometer and tube as those used previously, viz., a spectrometer of the photographic type and an X-ray tube emitting CuKα radiation. The X-ray beam was limited by a single slit parallel to the spectrometer axis, and by the area of the reflecting surface of the crystal. An undistorted crystal with a reflecting plane on the spectrometer axis will give a reflected image of that portion of the focal spot—usually about 1 mm. in diameter—from which X-rays may pass to it through the slit. Distortion of the crystals giving rise to changes in inclination of the reflecting planes will affect the length of the reflected spot, whereas alterations of the lattice parameter will only effect a shift of the reflected spot corresponding to a change in reflecting angle for any given wavelength. A small camera, 3 cm. radius, was used for the study of crystal distortion, whilst a camera of 6 cm. radius as well as one capable of adjustment to larger radii was employed for the study of variations in the lattice parameter.

The microscopic examination was carried out hand-in-hand with the X-ray measurements. Each section was photographed at a low magnification ($\times 150$) as a check on the degree of deformation, and also at a high magnification ($\times 1000$) for the purpose of structural examination. The photographs at high magnification were taken with a 3 mm. oil immersion lens (N.A. 1·3) under vertical illumination.

It was found necessary to anneal the individual crystals after they had been cut. For this purpose a special vacuum furnace was constructed. It was made up from flat tungsten strip formed into a long narrow tube closed at one end, into which the specimen was inserted. The temperature was measured by means of an optical pyrometer.

(3) *Crystal Hardening.*

The measurement of variations in the rate of deformation under given stress conditions offered the simplest if not the only means of investigating the hardening produced by the deformation of these small crystals. It follows from the theory of the formation of symmetrical wedge-shaped fractures established previously and illustrated by crystal models *, that the area of the slipping planes at any stage

* Phil. Mag. xlviii. p. 800 (Nov. 1924).

of the deformation up to about 50 per cent. reduction of diameter will be approximately proportional to the local reduction of diameter perpendicular to the axis of the specimen and the line of intersection of the two sets of slip planes. Consequently in the case of a crystal deformed under constant load, the stresses on the slip planes will increase proportionally to this local reduction of diameter. Measurements on the rate of deformation under these conditions should therefore yield information concerning any variation of slip resistance which may occur during the different stages of deformation.

Crystals whose deformation process closely approximates to the theoretical are easily realized in practice, the main differences being due to crystal distortion and to slight alterations in the mean crystal orientation during the deformation process when the crystals were unsymmetrically inclined to the wire axis before deformation. The combined microscopic and X-ray study of such crystals described in the previous experiments showed that, although bendings of the crystal planes may amount to changes of inclination of more than 20°, the mean lattice orientation was within 10° of being symmetrical to the wire axis in all cases. Further, it appeared that crystals deforming symmetrically from the beginning would not alter appreciably in their mean orientation throughout the deformation process. Photographs fig. 2 (Plate II.) and fig. 3 (Plate III.) illustrate the slightly unsymmetrical and the symmetrical type of deformation respectively. It is clear that the distortion will tend to alter the relation between the maximum local reduction in diameter and the area of the slipping planes in the sense that the areas of these planes will tend to be larger than those calculated.

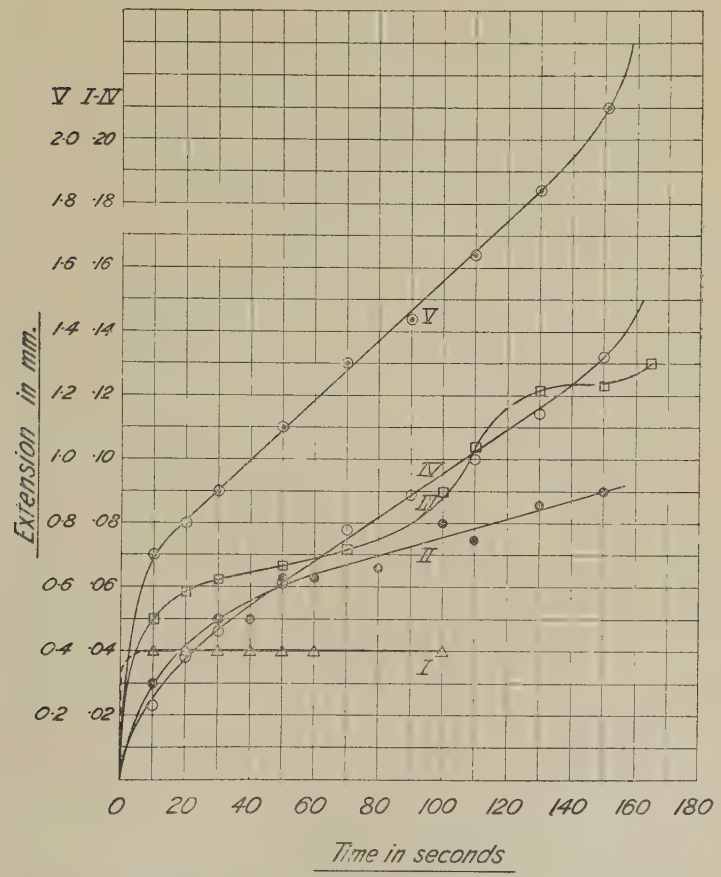
Measurements were made on the rate of decrease in the minimum crystal diameter for individual crystals in a large number of test wires when deformed under constant load at both 2000° K. and 1000° K. The loads in all cases were adjusted so as to produce fracture in times varying from one to ten minutes, the approximate values being calculated from the tensile strength temperature curves previously established*. The load was applied for equal increments of time at the given temperature and the local reduction of diameter measured after each application of the load. The results were plotted as local extension against time, the extension being calculated as 1·41 times the local reduction in diameter. The extension of the test wire as a whole was

* Phil. Mag. xlviii. p. 229 (Aug. 1924).

also measured in each case and plotted against the same time scale.

Typical curves for the 2000° deformation under a load of 80 gms. are shown in fig. 4. Curve I shows the rate of extension of a crystal so inclined * that the stresses on

Fig. 4.



one set of slip planes approached the maximum. In spite of this the deformation, which was rapid in the beginning, was reduced to zero. Curve II shows the rate of extension for a more symmetrically inclined crystal in which slipping

* The orientation of these crystals was judged by the shape assumed during deformation in accordance with the results recorded in fig. 36, p. 813, Phil. Mag. Nov. 1924.

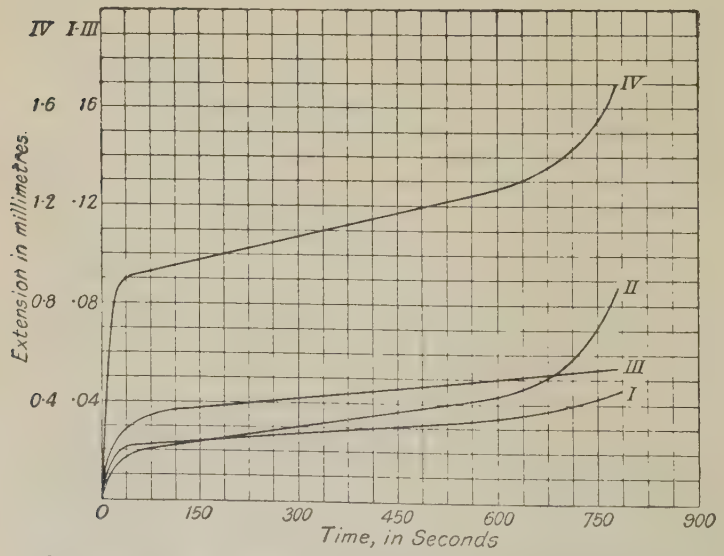
occurred on both sets of planes but more on one than on the other—the type shown in fig. 2 (Plate II.). In this case the deformation is not so rapid in the early stages, but is more rapid in the later stages than in I.

Curve III is an interesting and rather special case of a crystal which in the beginning was much like I, but in which owing to some favouring circumstances—possibly change of orientation—a second rapid increase in rate occurred followed again by a decrease in rate.

Curve IV is the normal time extension curve for a crystal deforming symmetrically from the beginning. It shows the smallest rate of flow in the early stages and the greatest in the later stages of deformation, and is the type which usually fractures; in fact this particular crystal actually did fracture, as indicated by the rise in the curve after the last plotted point.

Curve V shows the rate of extension of the test wire as a whole. It is obviously the sum of the deformations of the individual crystals of the more symmetrical type, although some crystals of the unsymmetrical type must contribute to the initial deformations.

Fig. 4*a*.

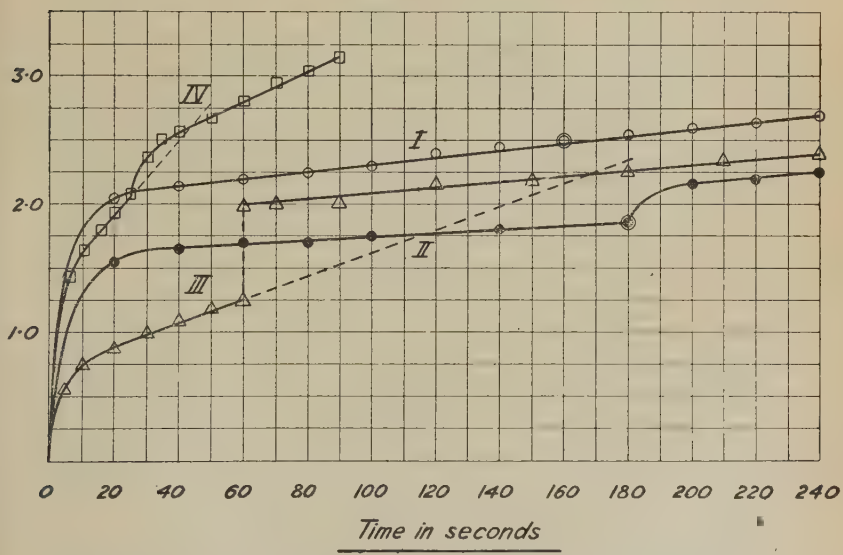


Curves fig. 4 *a* show a similar set of observations for crystals deformed at 1000° under a load of 300 gms. Curves I–III show the rate of extension of three symmetrically deforming crystals, and curve IV that of the

test wire as a whole. These curves show a change of rate which is greater than that taking place in similar crystals deformed at 2000°.

The most striking features of these curves are the rapid decrease of rate in the early stages of deformation and the marked tendency for the rate to attain a constant value in the later stages. The fact that there is a reduction of the rate in spite of increased stresses proves an increase in slip resistance or internal hardening of the crystal. The fact that deformation proceeds at a constant rate over a range of deformations in which the stresses on the slip planes must also increase at a constant rate, shows that the slip resistance under these conditions is also increasing at a constant rate.

Fig. 5.



The fact that the rate of extension of the test wire as a whole reflects the rate of the individual crystal, was utilized in studying further the effect of various factors on the degree of hardening ; for instance, the effect of annealing and the effect of rate of deformation.

Curves fig. 5 show some typical examples of such measurements. Curve I shows the rate of extension curve of the test wire under constant load when deformed at 1000°. After the initial rapid deformation the rate of flow becomes absolutely constant. At an extension of 2·5 mm. the wire was heated to 1000° for a period of two minutes

under no load and the original load again applied. The fact that the rate is unaltered shows that this heating has produced no measurable effect on the hardness. On the other hand, heating a similar wire to 1500° for the same time does remove some of the hardness, as shown in curve II. Curve III shows the effect of a rapid extension under an increased load for a very short time, the temperature of deformation being 2000°. The rate of flow under the original load is considerably reduced, which shows that the rapid deformation under increased stress produces a permanent hardening which must extend to unslipped portions of the crystal. The same effect may be produced by annealing at the temperature of the test—viz. 2000°—under no load and then applying the original load; the hardening is in this case increased without materially increasing the stress. This points to the rate of deformation as an important factor in the hardening process, although in each case the deformation is accompanied by increasing stresses.

The results of these measurements suggest that the straight line characteristic is due to some equilibrium between the three factors stress, temperature, and rate of deformation in their effect on crystal hardening. Similar conclusions to these have been reached by Polanyi and Schmid * working with tin single crystals.

(4) *Removal of Hardness.*

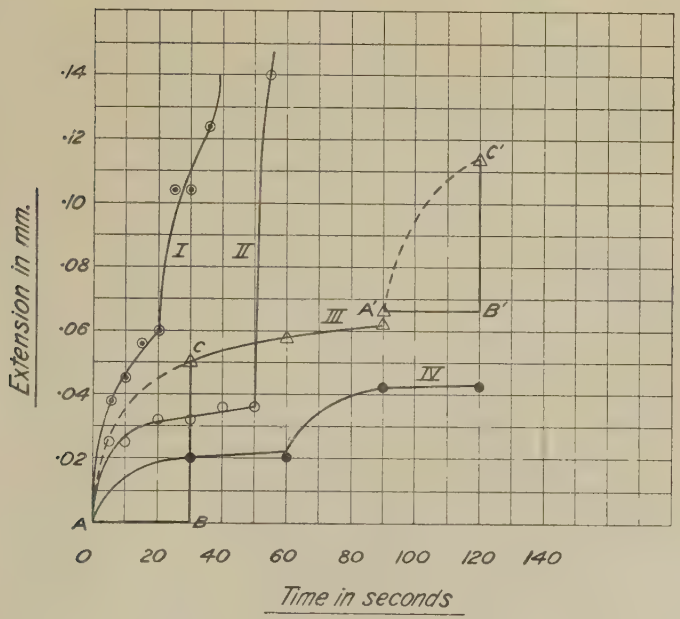
A quantitative estimate of the removal of hardness by annealing may only be obtained from measurements on the rates of flow of these crystals, provided that there is no change in mean crystal orientation during the annealing. Experiments to be described later clearly prove that this in fact is the case. The complete removal of hardness implies that equal stresses on the slip planes would produce equal flow velocities. We may therefore measure the rate of flow of a crystal under given initial stress conditions, allow the crystal to harden up as evidenced by a new reduced rate of flow, then anneal and reduce the stress in proportion to the degree of deformation and again measure the rate of flow; a comparison of the new rate with the original should give a measure of the hardness removal.

Preliminary measurements showed that a temperature of 2500° K. for 2 minutes was sufficient to remove the major portion of the hardness. Typical measurements are shown

* M. Polanyi and E. Schmid, *Zeit. für Physik*, xxxii. p. 684 (1925).

in the curves I–IV, fig. 6. Curve I shows the effect of annealing a crystal deformed at 2000°. After an extension of 0·06 mm. the curve repeats itself on adjusting the stress. Curve II shows the effect of leaving on the original load after annealing; a very much greater rate of flow than the original rate is produced by the increased stress, although this is only increased by 10 per cent. Curves III and IV

Fig. 6.



were obtained with crystals deformed at 1000°. After annealing the mean flow velocity $\frac{C'B'}{A'B'}$, Curve III, is nearly equal to the initial velocity $\frac{CB}{AB}$, the ratio of the two being 0·95. Curve IV shows how the curves may be made to repeat themselves under readjusted stress after annealing. The results of a number of measurements on crystals deformed at 1000° and annealed at 2500° for 2 minutes are given in Table I. They show that the initial mean velocity of flow after annealing is on the whole less

TABLE I.

Before Annealing.				After Annealing.		Ratio of mean initial velocity before annealing to that after annealing.	
Applied Stress. Kg/mm².	Initial mean velocity. mm /sec. $\times 10^{-3}$.	Constant Rate $\times 10^{-3}$.	Local Reduction. Area per cent.	Applied Stress. Kg/mm².	Initial mean velocity. mm./sec. $\times 10^{-3}$.		
10·0	0·7	0·03	8	10·0	0·7	1·00	
10·0	2·7	0·35	22	10·0	2·3	·85	
10·8	1·67	0·18	23	10·9	1·63	·98	Average ·86
10·7	0·9	0·03	15	10·6	0·63	·70	
10·8	1·4	0·03	19	10·8	1·30	·92	
10·0	1·53	0·03	21	10·1	1·13	·75	

than that before annealing by about 15 per cent. This probably does not mean that this degree of hardness is retained, as it has already been pointed out that there will be a tendency to adjust the new stress to too small a value owing to the crystal distortion. We may therefore consider that the hardness has been practically all removed by this annealing.

(5) *Crystal Distortion.*

The crystallographic nature of the distortion produced by the deformation of these crystals as well as the X-ray method employed in its measurement have already been described *. This distortion could only be explained as resulting from a break up of the crystal into fragments arranging themselves on curved surfaces which gave rise to an elongated reflected spot when a section of the deformed crystal was placed in a definite relation to the X-ray beam. For example, a section perpendicular to the wire axis through a wedge-shaped crystal fracture showed an elongated reflected spot when the minor axis of the section was mounted at the axis of the X-ray spectrometer, but no elongation was produced when the same section was mounted with its major axis in the same position. It appeared desirable to test the extent of this distortion at different stages of deformation of the symmetrically deformed crystals which have been investigated from the point of view of hardening and to study the effect of annealing.

Crystals in various stages of deformation were selected from test wires deformed under constant load at both 2000° and 1000° K. Sections were cut perpendicular to the wire axis in the region of greatest deformation, the wires in this case being mounted in hard glass. These sections were polished, etched, and examined for maximum distortion.

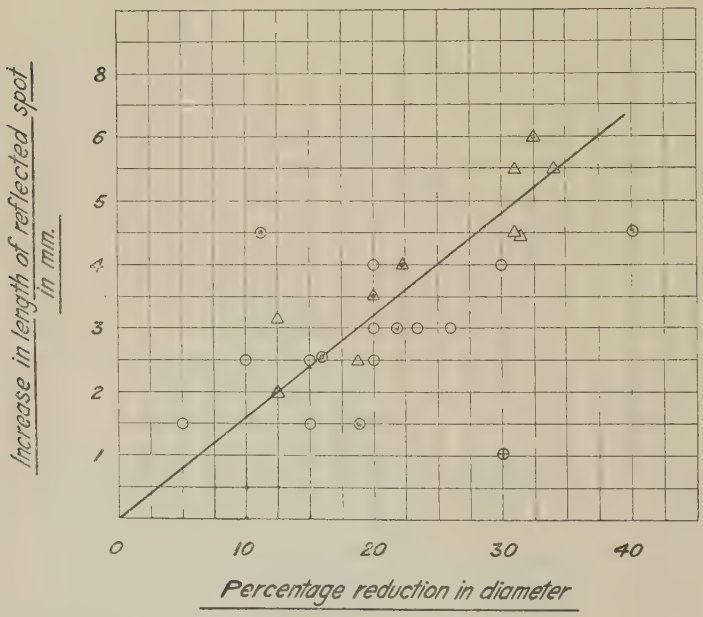
Photographs figs. 7 and 8 (Plates II. & III.) show typical sections of crystals deformed at 2000° and 1000° respectively. Below these, figs. 9 and 10 are photographs of the X-ray reflexions (× 2) obtained from the corresponding sections. They show a length of arc—due to a spreading of the X-ray beam—which is several times the length of the normal spot. It is to be noted that the arc is discontinuous in the case of fig. 9, whereas it is continuous in fig. 10.

The results of a number of measurements in terms of the increased length of the reflected spot in mm. are shown plotted against the percentage reduction in diameter in

* Phil. Mag. xlviii. p. 800 (Nov. 1924).

fig. 11. Although the observations are somewhat scattered there is clearly a correlation between the distortion and the degree of deformation, the distortion increasing in direct proportion to the degree of deformation. Further, the extent of the distortion appears to be the same for both types of crystal. In no case was the elongation of the spot zero, which proves that the distortion is distributed throughout the volume of the crystal in the region where slip is occurring.

Fig. 11.



The extent of the distortion may be estimated in terms of the radius of a continuous curvature sufficient to cause the measured increase in length of arc. Calculations taking into account the dimensions of the specimen and the constants of the spectrometer show that a 6 mm. increase in length would be caused by a continuous curvature of about 0·7 mm. radius; this would represent a minimum curvature consistent with the actual reflexion.

The effect of annealing was tested by heating the test wire to 2500° for 2 minutes under no load after the required deformation. Examination of a large number of such

annealed symmetrical crystals showed distortions in every way comparable with those produced in the unannealed crystals, the mean orientations being still symmetrical to the wire axis.

A few of the observations are plotted in fig. 11, the dotted circles representing annealed crystals which had been deformed at 1000° and the dotted triangles those deformed at 2000° K. A typical section of the latter type is shown in fig. 12 (Plate II.). Below, in fig. 13, is the corresponding X-ray reflexion; the arc is again discontinuous and of quite the same character as that of the unannealed specimen shown in fig. 9.

Owing to the divergence in the measurements of distortion as between one specimen and another, it appeared desirable to compare the distortion in the same specimen before and after annealing. For this purpose the special annealing furnace described in Section 2 was devised. No alteration of the spread could be detected as the result of annealing a number of such specimens at 2500° for a period of two minutes. Repolishing and etching so as to remove the old surface failed to produce any marked change other than that which would be expected on repolishing an unannealed specimen. Figs. 8 and 9 (Plates II. & III.) are photographs of the same crystal before and after annealing. The unannealed specimen was in this case copper-plated in order to avoid any heating during the preparation of the section, and the section was repolished and etched after annealing. Figs. 10 and 15 (Plate III.) show the corresponding X-ray reflexions. It is clear that this distortion is retained after annealing.

It is of interest at this juncture to record the effect on crystal distortion of a process of repeated extension and annealing, the stress being reduced after each annealing as in the case of the curves, fig. 6. The distortion of a crystal deformed in this way is plotted in fig. 11 as a crossed circle; it is clearly much less than a crystal extended the same amount under greater stresses. This would tend to show that the distortion is much more to be connected with the concentration of stress than with the mere process of deformation.

The fact that these crystals may be annealed at a high temperature without alteration of either orientation or distortion is in line with the results of experiments by Koref *, who has shown that fine tungsten single crystal wires may

* F. Koref, *Zeit. für Metallkunde*, Bd. xvii. p. 213 (1925).

be hardened by drawing and then annealed without any visible recrystallization.

(6) *Resolution of* CuKα *Doublet.*

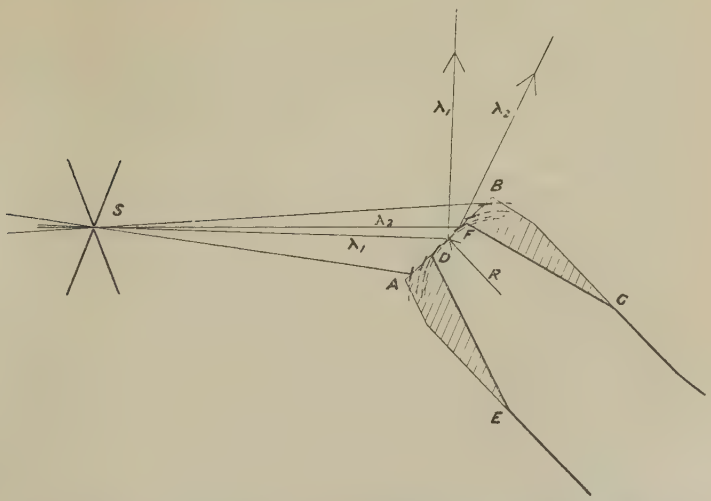
The extent of the distortion produced in these crystals suggests the desirability of measurements on the comparative resolving power before and after annealing. The resolving power may be diminished either by fineness of crystal size as shown by Debye and Scherrer, or by a lattice strain giving rise to a variable atomic spacing. The high degree of curvature into which these crystals have been deformed indicates a break up of the crystal into fragments which may be exceedingly small. The limiting size under these conditions will be determined by the degree of strain which the crystal lattice will stand without breaking up. It is fair to assume that this strain will not be greater than that corresponding to the elastic limit of the material, and it may be much less. This strain in the case of the pure tungsten crystal deformed at 1000° is only 0·025 per cent., the calculation being based on special measurements of Young's modulus and the elastic limit at this temperature. On the other hand, the lattice strain corresponding to the elastic limit of a Pintsch single crystal wire will be 0·18 per cent. according to van Arkel. The former is probably below the limits of accuracy of present day X-ray methods but the latter is not, as van Arkel has demonstrated by the use of very fine wires. It seemed worth while to compare the resolving power of these pure tungsten single crystals with that of Pintsch single crystals deformed (in a similar manner) at room temperature as a check on the elastic strain hypothesis. Should the pure tungsten crystals show a diminished resolving power which is comparable with that of Pintsch crystals, it would be fair to assume that its cause was crystal break-up rather than lattice strain, in which case an increase in resolving power on annealing must be associated with a coalescence of these small crystal fragments.

The symmetry and degree of distortion produced in wedge-shaped fractures suggest a suitable arrangement for obtaining good resolution of a monochromatic X-ray beam. It has already been pointed out that the distortions in such wedges are crystallographic in nature. They are such that the (110) planes of adjacent fragments tend to lie on approximately coaxial surfaces the axis of which is perpendicular to the wire axis and parallel to the wedge

edge, the surfaces being convex towards the wedge edge. This is shown diagramatically in fig. 16.

A B represents a section of the wedge cut at right angles to the wire axis. The dotted lines represent the concentric surfaces which intersect the plane of A B at angles which vary as shown. It is clear that an X-ray beam composed of one wave-length λ_1, and divergent from a slit S, will only reflect from a narrow portion of the section at D when A B is fixed at the appropriate angle for the reflexion of λ_1. A second wave-length λ_2 will be reflected from a second portion of the section F which makes the appropriate angle of reflexion for the corresponding part of the X-ray beam.

Fig. 16.



Suitable conditions for the comparison of the resolving powers of both the pure tungsten and the Pintsch single crystals were realized in practice. Crystal wedges (Pl. V. fig. 17) were obtained on fracturing Pintsch wires at room temperatures. These were quite comparable with those obtained by fracturing the pure tungsten wires at 1000° (fig. 18). Annealing the specimens produced no marked effect on the crystal distortions, which in all cases were symmetrical with the wire axis, and which amounted to a gradual change in inclination of the (110) planes through at least 20° in the case of the pure tungsten crystals and 10° in the case of the Pintsch crystals. Typical sections through these wedges are shown in figs. 19–22. Fig. 19 is from an

unannealed specimen of pure tungsten prepared by mounting in copper. Fig. 20 is from a similar specimen which had been annealed at 2500° for two minutes, then mounted in hard glass. Figs. 21 and 22 (Plate V.) are from the same Pintsch wire before and after annealing respectively. Below these in figs. 23–26 (Plates IV. & V.) are photographs of the spread in the X-ray beam obtained from the corresponding sections.

The resolving powers of two crystals such as those in figs. 19 and 20 (Plate IV.) were compared by mounting the sections side by side with their major axes on the axis of the spectrometer using Cu Kα radiation. Exactly similar reflexions giving a well resolved doublet were obtained in all such cases. Fig. 27 is a photograph of typical reflexions enlarged five times.

The accuracy of lining up of the two crystals does not permit comparison of the absolute magnitude of the atomic spacing, but it may be claimed that there is no measurable difference in line breadth in the two cases. Comparing the resolving power of Pintsch single crystals before and after annealing always showed a non-resolved reflexion before annealing and a well resolved reflexion after annealing. The two photographs in fig. 28 (Plate V.) are typical of such reflexions. The increase in line breadth necessary to cause the non-resolution must correspond to a change of reflecting angle of at least 0·05 per cent. and probably more.

In order to be sure that the fuzziness was not produced by some alteration in crystal distortion too small to effect the spread and which would reduce the reflecting surface on annealing, a number of crystals in the hard state were ground in such a way as to limit the reflecting surface to a long narrow zone about 0·02 mm. in width *, the crystal being ground to a chisel-edge as shown by the unshaded portion in fig. 16.

Mounting these edges on the spectrometer axis and rocking produced non-resolution in all cases until after the crystals were annealed, they then resolved as they should.

In order to test for any possible shift in the mean atomic spacing due to the deformation process, a precision measurement of the mean reflecting angle for the reflexion of the Cu Kβ line was made before and after annealing. No measurable change was observed within the limits of experimental error, which was probably under 0·05 per cent.

* The spectrometer arrangements were such that a surface ·02 mm. in width rocked at the axis was sufficiently small to give good resolution. This was actually tested by mounting a recrystallized wire of this dimension on the spectrometer axis and rotating through several degrees; good resolution was easily obtained.

(7) *Microscopic Examination.*

The chief results of the microscopic examination, which was carried out hand in hand with the study of distortion by the X-ray method, will now be considered.

The crystals deformed at 2000° gave discontinuous X-ray reflexions which showed that the crystal had been broken up into relatively large fragments or groups of fragments even before annealing. Microscopic examination confirmed this conclusion and gave additional information in regard to the nature of the break up. It showed that the break up was crystallographic in nature in the sense that boundaries tended to lie along definite crystal planes. The boundaries appeared in all cases as lines parallel to the major axis of sections cut perpendicular to the wire axis, and therefore correspond to lines of intersection of two sets of (112) slip planes. It was more difficult to detect their direction in planes cut perpendicular to these sections along lines parallel to their minor axes, although in extreme cases it could be seen that they did not follow the slip plane as might be expected, but rather appeared as irregular splits more nearly inclined at 45° to the wire axis. Photographs figs. 29–30 (Plate IV.) illustrate this point. Fig. 29 is from the same annealed crystal as that shown in fig. 12, which clearly shows the vertical lines of break up in the planes perpendicular to the wire axis. Fig. 30 is from a similar unannealed crystal cut in a plane perpendicular to this section and to the vertical boundary markings. The line connecting the projecting portion of the crystal in the upper left-hand corner with the niche in the lower right-hand corner of the photograph is the trace of the (112) plane on which a large slip or series of slips has occurred—such as can be seen in fig. 2. There is no indication of a boundary marking extending in this direction, but the long marks inclined at about 45° and ending in this niche doubtless are the boundary markings in this case. Results such as these rather point to the conclusion that the deformation process is accompanied by a type of recrystallization at this temperature.

Crystal wedges produced by the fracture of single crystals at this temperature show this break up in a very marked degree. In sections of such crystals cut perpendicular to the wire axis as many as 10 vertical markings have been counted and the X-ray reflexion has shown as many as 15 discontinuities in some cases. The number and character of these is unaffected by annealing.

No such obvious evidence of break up occurs in the case of crystals deformed at 1000°, although in the extreme

case near the tip of crystal-wedge fractures one or two markings are to be found which are similar to those found in the 2000° wedges. These crystals, however, show very marked differences in etching effects before and after annealing. Although the character of the etch markings remains unchanged, a marked differential rate of etching—evidenced by differences in level—occurs in the case of the unannealed crystal which does not occur on repolishing and etching after annealing. The effect is also most marked in the case of the crystal wedges. Photographs 31–34 (Plates III. & IV.) illustrate this. Figs. 31 and 32 are of the sections shown in fig. 8 and fig. 14 (Plate III.) respectively. Figs. 32 and 34 are sections of the same crystal wedge before and after annealing respectively—the crystal having been repolished and etched after annealing. It is to be noted in this case, that although the differences of level occurring in fig. 33 do not occur in fig. 34, the change in orientation of the lamellæ is just as marked in the annealed specimen as in the unannealed, which confirms the results of the X-ray measurements of distortion.

The Pintsch single crystals showed no marked difference before and after annealing, which is probably due to a masking of the effect by the thorium oxide present in these wires. Figures 35 and 36 (Plate V.) are from the same crystal before and after annealing. The larger number of black dots in figure 36 has probably not been produced by the annealing, as a number of sections of unannealed crystals showed similar markings.

(8) *Discussion of Results.*

The chief interest in the results of these experiments lies in their bearing on the theories of hardening accompanying deformation and the possible existence of residual lattice strain in a worked metal.

The most important results appear to be the persistence of crystal distortion after annealing and the improvement in resolving power on annealing distorted Pintsch single crystals. The former implies a broken up state which is not altered sufficiently by annealing to re-establish a new perfect single crystal and that the break up is not, therefore, the cause of hardening. If we accept this view, it suggests that the cause of the production of fuzziness is the cause of hardening even though it may only be measured in extreme cases.

The cause of fuzziness—as in van Arkel's experiments—is limited either to the size of fragment into which the crystal is broken up or to a disorganization of the crystal lattice

within the broken up fragments. The size of crystal required for a broadening of line equivalent to a variation in reflecting angle of 0·1 per cent. would be of the order 10^{-5} cm. as calculated from the theory of Debye. Although it would be difficult to prove that the broken up fragments are not as small as this in the case of the Pintsch wire, the experiments on the pure tungsten crystals indicate that there is a tendency toward lattice preservation which would render it improbable. The 2000° deformations produce a break up which can be seen under the microscope and the 1000° deformations do not produce a break up sufficient to give non-resolution of the Cu Kα doublet, although the crystal distortion appears to be sufficient to do this were no other cause operative in maintaining lattice continuity *. On the other hand, we have the agreement between the degree of fuzziness and the strain corresponding to the elastic limit for two cases of the same material. The results, therefore, point to elastic strain rather than crystal size as the cause of fuzziness.

Viewed in the light of elastic strain as the cause of increased slip resistance, the rapid increase of hardness in the early stages of deformation would be accounted for by the early setting in of a distortion which involves a bending of the crystal fragments as well as the production of lattice discontinuities. These bendings would involve equal amounts of extension and compression, which is in agreement with the X-ray measurements. The building up of the progressively increasing curvatures without progressive increase in hardness could be accounted for without assuming that the strain in these fragments increases in proportion to the degree of deformation, as the degree of break up can be brought in to account for this. It is to be expected that the degree of strain would increase with increase of stress, which is in accord with the fact that hardness increases with increase of stress under conditions of constant rate of deformation. The effect of time and temperature on the degree of hardness would appear to be associated with the tendency of the lattice to maintain itself in the unstrained state, the extent of the restitution depending on the temperature and the degree of strain. The differences in rate of etching before and after annealing would on this view be associated with differences of residual elastic strain.

* The radius of curvature of the distorted crystal may be as small as 0·02 mm. Crystal lamellæ bent to this radius cannot be thicker than 2×10^{-5} cm. if they show no change of atomic spacing exceeding 0·025 per cent.: viz., the measured value. This is of the order of magnitude required by the theory of Debye for non-resolution of the Cu Kα doublet.

XXIII. *Improved Grating for Vacuum Spectrographs.* *By* R. W. Wood *and* Theodore Lyman *.

[Plate VI.]

ONE of the difficulties attending the use of concave gratings in vacuum spectrographs is the oxidation or corrosion of the polished metal surface by active vapours from the discharge-tube. This can be in part prevented by constructing the spectrograph in such a way that the vapours are pumped out through a port immediately behind the slit (T. Lyman, 'Astrophysical Journal,' lx. p. 1, 1924).

The suggestion was made by one of us in a note published in this Journal in September 1924 that glass gratings would be found more suitable than metal, as they could be cleaned without difficulty. One such grating of one half metre radius had been successfully ruled and etched at the time, but it was destroyed by fire before any tests were made with it. The original plan was to coat the glass grating with a film of metal by cathode discharge. This film could be easily renewed from time to time, if necessary. On discussing the matter, however, shortly after the publication of the paper above referred to, we came to the conclusion that it would very probably turn out that the surface of the glass would have a reflecting power superior to that of metals in the region of the shortest wave-lengths. This surmise we based on the fact that the decreasing reflexion coefficients of metals and the increasing coefficients of transparent substances (with decreasing λ) practically meet in the neighbourhood of wave-length 2000.

Pressure of orders for speculum gratings have kept the two dividing engines of Johns Hopkins University so busy that it was not until this spring that experiments with glass gratings were commenced again.

Three have been made already, two four-inch ones of one metre radius, and a five-inch one of two metres radius. They were ruled with a very light pressure of the diamond to avoid the wear which inevitably destroys the ruling-point if it is operated under sufficient pressure to secure brilliant spectra, and then etched by the method described by one of us (R. W. Wood, "Intensification of Glass Gratings, Phil. Mag., December 1906) twenty years ago.

* Communicated by the Authors.

The concave mirror showed practically no spectra at all when it came from the ruling engine. In bright sunlight it was just possible to see the ruled surface, which is probably traversed by extremely narrow deep cracks. Dilute hydro-fluoric widens these by eating away the edges, and produces a corrugated or undulating surface which gives bright spectra. Too much etching causes a diminution of the brilliancy. To obtain the proper amount of etching to give the maximum brilliancy the same method was employed as that described in the paper referred to above—namely, to dip one corner of the grating into the acid to the depth of about 3 mm. for five seconds, and then wash and dry it. On examination the etched corner is found to be much brighter than the rest of the surface. The whole grating surface is now immersed face down in the acid for five seconds, washed, dried, and again examined. It now shows the same brilliancy over its whole surface as that exhibited by the corner in the first instance, but the corner is usually found to be much brighter than the rest. A third bath of five seconds is given and the process repeated until the whole surface has been brought up to the brilliancy of the corner. This is the point at which to stop, as further etching produces no improvement and eventually weakens the intensity.

One of the glass gratings of a metre radius has been tested in a vacuum spectrograph at Harvard. The ruled surface measures 5×8 centimetres, there are 15,000 lines to the inch. Spectrograms obtained in the first order of a concave grating ruled at Johns Hopkins on speculum served as a means of comparison. This speculum grating was almost identical in dispersive power with the instrument under test, though its ruled surface was not quite so large, measuring $3{\cdot}1 \times 7{\cdot}8$ centimetres. It differed also from the glass grating in that it possessed a strong second-order spectrum. It had been in continuous use in the vacuum spectrograph for more than 18 months, but showed little decrease of reflecting power in the extreme ultra-violet—a fact interesting in itself.

The region examined extended from 1900 A.U. to the limit of the spectrum. For the upper part of this range a hydrogen discharge-tube was employed, while on the short wave-length side of 1300 A.U. a vacuum spark, either between copper or tungsten terminals, was used.

It is impossible to say anything very definite as to the relative efficiency of the two gratings between 1900 and 1300 A.U., for in this region it was necessary to compare

two sets of spectrograms taken on plates of quite different photographic behaviour, and at dates separated by nearly a year. It appears probable, however, that on the long wave-length side of 1400 A.U. the speculum grating has the advantage.

On the other hand, a very positive statement may be made concerning the behaviour of the two instruments in the range between 1300 A.U. and the limit of the spectrum, for in this region all spectrograms were obtained under the same conditions and on dates separated by but a few days.

As a result of these experiments, there can be no doubt whatever that the glass grating produces a much more intense spectrum on the short wave-length side of 500 A.U. than that obtained from speculum. This superiority is particularly pronounced in the region of the very shortest wave-lengths between 300 and 200 A.U.

It appears, therefore, that glass gratings will prove very useful in vacuum spectroscopy, since their reflecting power for light of very short wave-lengths is higher than that of similar instruments ruled on speculum and is not likely to change with time.

Thus far only a grating of 15,000 lines to the inch has been tested in the vacuum spectrograph, but two of 30,000 lines have been ruled and etched, and appear to be satisfactory. Experience has shown that gratings ruled with the 30,000 spacing on speculum metal are very much less brilliant in the region of very short wave-lengths than the 15,000 gratings. This is probably due to the complete removal of the polished surface. In the case of the glass gratings it is expected that this trouble will not be found, as the etching process probably gives the same type of undulating surface in both cases.

The spectra in Plate VI. were taken with the high vacuum spark between copper terminals. The upper spectrum was made with the speculum grating, the lower was obtained with the grating on glass. The time of exposure was the same in both cases.

The relatively great intensity of the violet region in comparison with the red, in the case of the glass gratings, is very marked when the grating is held in sunlight, and the spectrum focussed on a white screen.

XXIV. *On the Origin of the E.M.F. of a Photoelectric Cell, containing a Fluorescent Electrolyte.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

I WISH to make some remarks suggested by the very interesting work of Mr. W. Rule (Phil. Mag. (7) i. p. 532) on the variation of the E.M.F. of photoelectric cells containing a fluorescent electrolyte, when the amount of the fluorescent material is changed.

Mr. Rule admits that the electrometric measures furnish always the value of the E.M.F. of adsorption, and neglects thus the Becquerel effect which, as I have pointed out (*Comptes Rendus*, t. clxxvii. p. 395, 1923), is superposed on the latter, chiefly in the cells provided by very concentrated fluorescein.

Each E.M.F. measured is also the algebraic sum of two quantities varying in different ways with the illumination time; so are explained the inflexions presented by the curves of Mr. Rule, when the concentration is great.

In his experiments, the E.M.F. attains a constant value in 40 minutes, but in dilute solutions; however, it is possible to separate the effect produced in the mass of the liquid by screening the light; the maximum reached by the E.M.F. in darkness is independent of the initial electrical conditions of the experiment (*Comptes Rendus*, t. clxxx. p. 1102, 1925; *Soc. Française de Physique*, No. 217, p. 73 s, 1925).

For the same reason, I do not see any discrepancy between the absence of an E.M.F. in a cell containing a pure sodic solution only, and the existence of an E.M.F. produced by the light emitted by a very fluorescent solution itself, which illuminates the electrode protected against the direct light of the quartz lamp. It is a Becquerel E.M.F. whose sign is contrary to that of the new effect I have described, and which is the subject of Mr. Rule's research. A proof of this is that the positive E.M.F. in the contested experiment vanishes in the darkness and the negative effect subsists alone.

Moreover, I will remark that a cause of mistake in the measures of conductivity of fluorescent electrolytes is to be found not only in the Becquerel effect, if an electrode is illuminated, but also in the E.M.F. produced by the illumination of the liquid mass which arises if the apparatus is not disposed in a strictly symmetrical manner in the light pencil.

Yours faithfully,

A. GRUMBACH.
Professeur à l'Université de Nancy,
Institut de Physique.

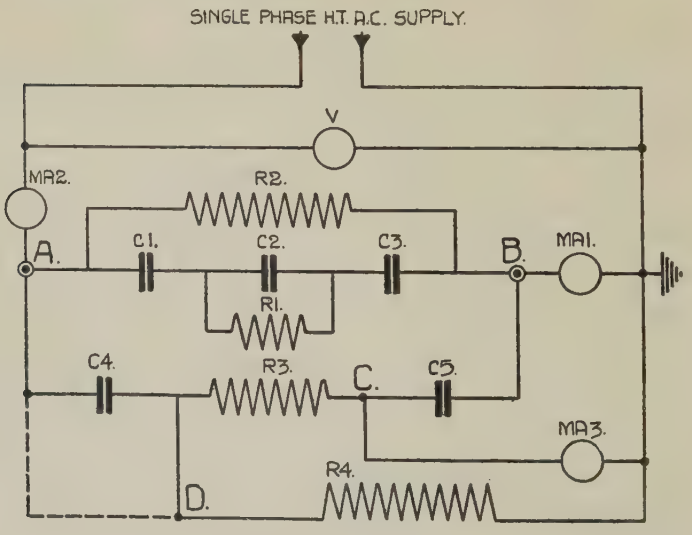
Nancy, France.
June 11, 1926.

XXV. *On the Determination of the Current Voltage Characteristic of a Siemens Ozonizer.* *By* R. Winstanley Lunt, *M.Sc., Ph.D.*, 1851 *Exhibition Senior Student* *.

WHEN using a Siemens ozonizer, that is to say an ozonizer formed from concentric cylinders of glass or other insulator, it is not infrequently desirable to cool either one or both electrodes in order to reduce thermal effects to a minimum.

This is most simply achieved by allowing a stream of tap-water to flow through a thin-walled glass vessel in contact with, or immersed in the mercury or other conducting material constituting the electrodes. When such a device is employed considerable care must be exercised in choosing the electrical connexions appropriate to the determination of the true current flowing through the ozonizer and the voltage associated with it.

A typical circuit in which an ozonizer is connected to a source of high-tension alternating current is represented, using the usual conventions, in the following diagram.



The ozonizer is represented by three capacities in series †, the capacity C_1 of the inner cylinder of dielectric, the

* Communicated by Prof. F. G. Donnan, F.R.S.

† *Cf.* Phil. Mag. xlix. p. 1238 (1925).

capacity C_2 associated with the annular space containing the gas subjected to the discharge being in parallel with a resistance R_1 representing the inverse of the conductivity of the gas due to gaseous ionization, and the capacity C_3 of the outer cylinder of dielectric. A and B denote the electrodes.

The glass or other insulating surface separating the electrodes possesses a leakage resistance represented by R_2, which may easily be maintained of the order of 10^2–10^3 megohms, so that this leakage current is in general negligible.

The column of water connecting the tap, or water supply, to the high-tension electrode A through C_4 offers a leakage resistance denoted by R_4.

A glass vessel carrying cooling water in contact with the high-tension electrode A is associated with a capacity C_4 in series with a resistance R_3 which arises in the stream of cooling water flowing between the electrodes. Similarly, the glass vessel in contact with the low-tension electrode introduces a capacity C_5 between the cooling water and this electrode.

If the circuit be not earthed at the point C, then the system C_4, R_3, C_5 forms a current path in parallel with the ozonizer; the current read by the milliameter MA_1 is therefore greater than that carried by the ozonizer. It has been found that the error due to this current is not generally negligible.

A convenient method of earthing the circuit at the point C has been achieved by allowing the stream of cooling water to flow through a short length of copper tubing immediately before entering the cooling vessel immersed in, or in contact with, electrode B. To this copper tubing is soldered a lead connecting to earth. The potential across C_5 is thereby reduced very nearly to zero, and is due solely to that arising from the current through MA_1 and the resistance of that instrument. It is therefore of the order of one or two volts.

The voltage applied to the ozonizer is read on the high-tension voltmeter V.

In a number of experiments carried out in these laboratories, it has been observed that the total current in the high-tension line as indicated by the milliammeter MA_2 is equal to, within the limits of experimental error, the sum of the current flowing through the ozonizer as indicated by the milliammeter MA_1, that flowing through C_4R_3 indicated by

the milliammeter MA_3, and that flowing through R_4, thereby indicating that no sensible current flows through C_5.

It may not be out of place to mention two methods that have been found to obviate a difficulty that arises in the cooling of the high-tension electrode. It is obvious from the diagram that unless the impedance of the capacity C_4 be much lower than the resistance R_3, the condenser C_4 will be subject to a strain due to the major portion of the impressed voltage. That is to say, the glass walls of the vessel carrying the cooling water to the electrode A have to withstand a voltage of the order of the applied voltage. In practice it has been found that frequently the dielectric strength of glass is inadequate to this stress. Satisfactory results can be achieved by constructing this vessel of fused silica.

An alternative method that is practicable when a silica vessel is not available consists in connecting the electrode A to the stream of cooling water, in the manner adopted at the electrode B, at the point of entry to, or exit from, the cooling vessel associated with the electrode A, represented on the diagram by D, a dotted line indicating this connexion. It is then necessary to arrange for a long and well insulated column of water to connect the cooling vessels in order that the current carried by this column may be conveniently small.

When it is necessary to determine the heat transferred from the high tension electrode to the cooling water, further precautions must be adopted. These consist in providing two short lengths of copper tubing, each connected to the electrode A, in the stream of cooling water. One is placed at the point where the stream enters the cooling vessel and the other at the exit therefrom. No appreciable current can then flow through the water in the cooling vessel. It is important to note that the thermometers which indicate the temperature of the stream must be introduced into the stream between each copper tube and the cooling vessel.

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XXVI. *A simple Vacuum Arc Mercury Still for Laboratories.* *By* H. P. Waran, *M.A., Ph.D., D.Sc., F.Inst.P., Additional Professor of Physics, The Presidency College, Madras* *.

MERCURY, so largely used in laboratories in connexion with so many experiments, gets contaminated very easily by contact with foreign materials rendering it unfit for further use until it is purified again. There are many ways of cleaning it, but none so satisfactory as distilling it *in vacuo*. The usual process so largely adopted of shaking it with dilute nitric acid or passing it as a fine spray through a column of dilute nitric acid, is not only very wasteful but the mercury requires further washing and drying before it is ready for use. Even then the product can never be regarded as so good as distilled mercury.

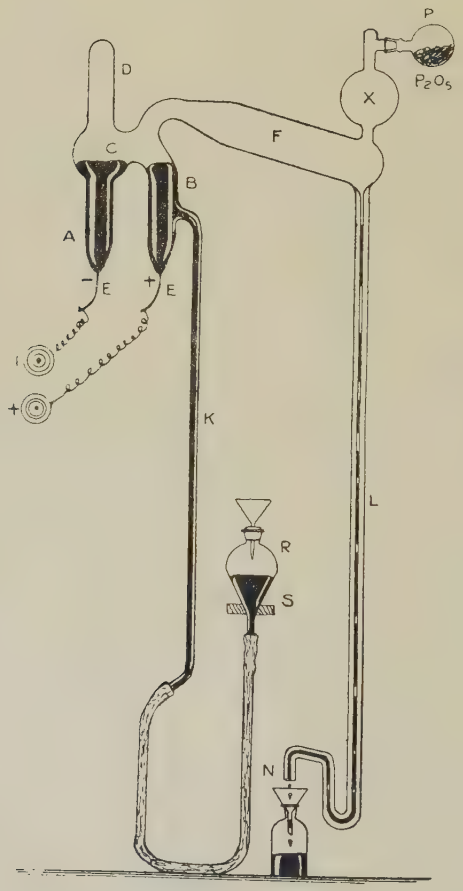
The distillation of mercury, like the distillation of any other liquid, can easily be done in retorts of iron or pyrex glass that can stand the temperature of 357° C., the boiling-point of mercury at atmospheric pressure. The distillation, if conducted *in vacuo*, yields a product distinctly purer, as the mercury will boil off at a very much lower temperature and thus be free from any volatile impurities that may come along with it at a higher temperature. To distil the mercury *in vacuo* there are many forms of apparatus on the market, but a very convenient form of it that has been found to be quite good is the one shown in fig. 1, and though the arc pattern of it is in no way new, still the present form has many other interesting and useful features as well to recommend it for general use in laboratories.

ACB is an inverted U-tube with sealed-in platinum electrodes E and E′. The limb A has a short vertical prolongation D, about ten centimetres long, which serves as an auxiliary condenser for the negative limb A. To the limb B is attached a large air-cooled condenser F formed out of a thin-walled tube about $1\frac{1}{2}$ inches in bore and about 8 inches in length. From the other end of F two tubes branch off. The vertically downward branch L is a capillary tube of not more than 2 mm. bore and over 100 cm. in length, bent round at the lower end as

* Communicated by the Author.

shown at N. The upward branch has a bulb, and it terminates in a conical ground joint to which a bulb P containing P_2O_5 is attached with vacuum grease. From the side of B there is a vertically downward tube K

Fig. 1.



about 70 cm. in length, and its lower end is connected to a mercury reservoir R by a 4 foot length of pressure tubing. The whole of the apparatus is mounted on a backboard of wood which is attached to a vertical wall in any convenient corner of the laboratory. The platinum

electrodes are soldered to lengths of copper wire leading to terminals on the board which are connected to the mains through a 10 ampere fuse and switch. An adjustable resistance is also included in the circuit so that the current may be adjusted within the limits of 8 and 4 amperes. This mercury arc still operates as follows.

The switch being off, the mercury reservoir R is raised until the mercury rising in B overflows into F. This thin stream of mercury breaks into drops on reaching the upper end of L, and during their passage down L these drops of mercury trap air from the system, and by a Sprengel pump action the system is rapidly exhausted. The mercury overflowing at the delivery end N is caught and poured back into R at this stage. In a few minutes a vacuum of the order of less than a tenth of a millimetre of mercury is reached inside the apparatus, the phosphorus pentoxide in P being essential to remove the water vapour liberated as the mercury and the glass walls get heated up under the arc. The mercury reservoir is now restored back to its shelf S and the current is switched on immediately. By the lowering of the mercury level in B, as the contact with the mercury in A is broken at C, an arc plays between the two pools of mercury in A and B and the mercury is rapidly vaporized, the amount evaporated from the negative limb being much less than that evaporated from the positive limb. A part of it condenses in D, and is returned to the limb A where the mercury remains for ever at a constant level. Much of the vapour, however, goes down into F, where by air-cooling it condenses and trickles down into L, where the Sprengel pump action continues to keep the condenser and arc space highly exhausted automatically, a condition necessary for the efficient working of the arc and the evaporation of the mercury at the lowest temperature. As the distilled mercury comes down L it displaces out the small quantity of dirty mercury that was in it. After returning the yield of mercury during the first ten minutes back into the reservoir, the mercury dropping out at N may be collected as dry distilled mercury of a very high degree of purity.

Once the arc distiller has been set up in this way and the vacuum sucked up by itself, all that one has to do is to pour in dirty mercury at R, raise the mercury reservoir a few centimetres to establish a momentary contact with A, and then restore it back to its shelf.

The breaking of the contact at C starts the arc, and the mercury distils over merrily and flows out at N in drops, the progressive fouling of the vacuum by the gases liberated by the dirty mercury being automatically pumped out by the Sprengel action at L.

One or two arc distillers of this type set up in physical laboratories have the great advantage that in addition to supplying pure mercury for accurate experimental purposes, the arc can also be used as a bright source of light for many optical experiments. In such cases, the distilled mercury is only a bye-product in the operation.

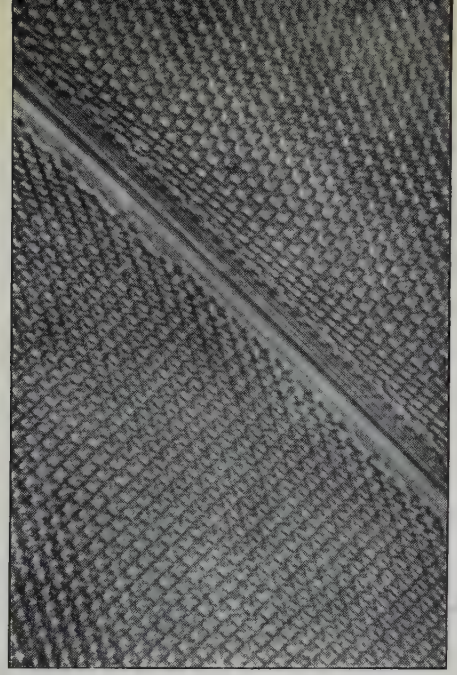
Arc distillers of this type are now being made and sold by Messrs. Baird & Tatlock (London) Ltd., 14–15 Cross Street, Hatton Garden, London, E.C. 1. Two distillers of this type in operation in my laboratory taking 5 amperes at 60 volts have been found to have an average yield of $1\frac{1}{2}$ lb. of distilled mercury per hour, or approximately 2 grms. of mercury per watt hour.

The yield can of course be increased by eliminating the auxiliary condenser D and fitting the negative limb also with a reservoir. In this case the platinum electrode seals E and E′ can be eliminated and the current introduced through the two reservoirs. Further, the condenser F can also be replaced by a water-jacketed one cooled by a circulation of water. The vapour pressure inside can thus be kept low even with a higher current through the arc with a corresponding increase in the output of distilled mercury per hour. But the arrangement is complicated and is not to be recommended for the average laboratory use.

Note.

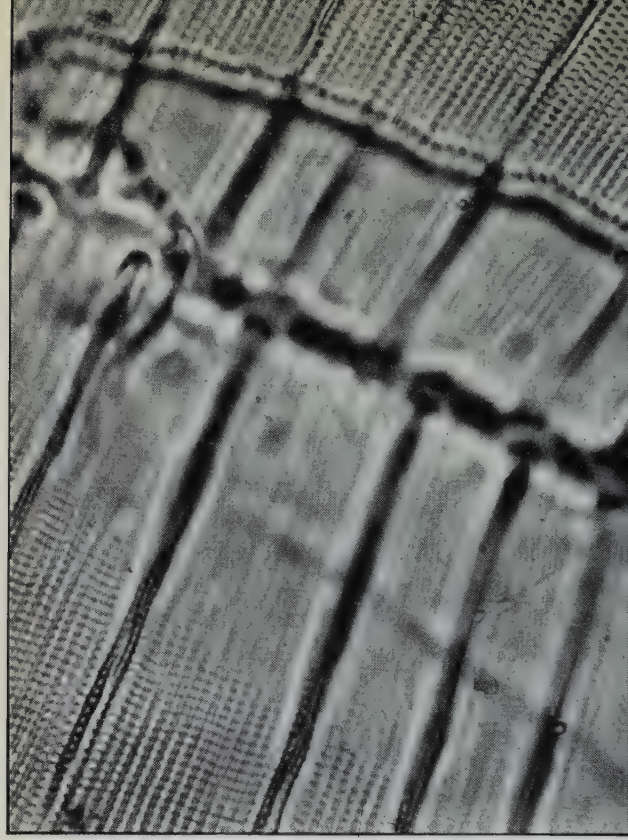
The Publishers regret the omission of Plate XVI. A, illustrative of Mr. W. Scutt's Paper "On Germanium in a British Mineral," in the May Number, vol. i. p. 1007.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



I. Pleurosigma angulatum.

Taken with Mg-line 280 $\mu\mu$; monochromatic objective, ap. 1·25; quartz ocular 20. Magnification: 3600.

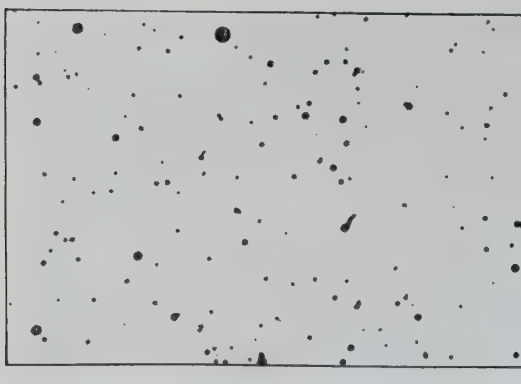


II. Surirella gemma.

Taken with Mg-line 280 $\mu\mu$; monochromatic objective, ap. 1·25 Magnification: 3600.

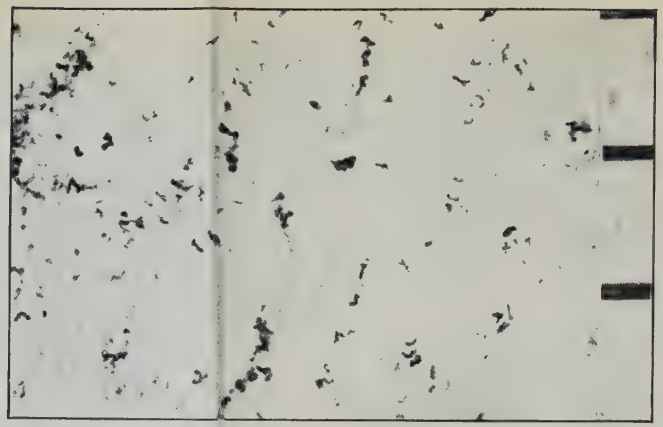
III. Selenium spheres.

Taken with Cd-line 275 $\mu\mu$; monochromatic objective, ap. 1·25; quartz ocular 10. Magnification: 1500. (Phot. Dr. A. Köhler.)



IV. Selenium spheres.

Taken with Cd-line 275 $\mu\mu$; monochromatic objective, quartz ocular 10. Magnification: 1800. 1 divis scale = 1.10^{-3} cm.



VII. Sulphide of Antimony (not spherical).

Taken with Cd-line 275 $\mu\mu$; monochromatic objective, n. a. 1·25; quartz ocular 10. Magnification: 1800. 1 division of the scale = 1.10^{-3} cm. (Phot. E. Sax.)

SPHERES.

$\mu\mu$; monochromatic objective, ap. 1·25;
on: 4300. 1 division of the scale = 1.10^{-3} cm.

VI. Mercury spheres.

75 $\mu\mu$; monochromatic objective, n. a. 1·25; quartz ocular 10. Magnification: 1800. 1 division of the scale = 1.10^{-3} cm.

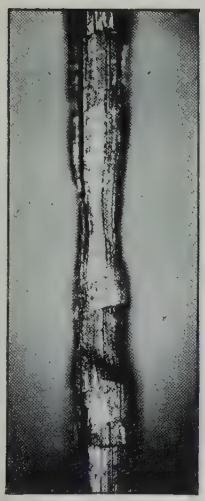


Fig. 2.

Fig. 7.

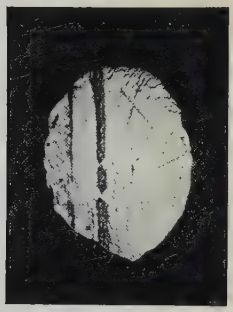
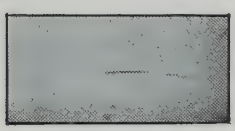


Fig. 12.



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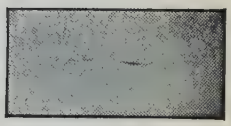

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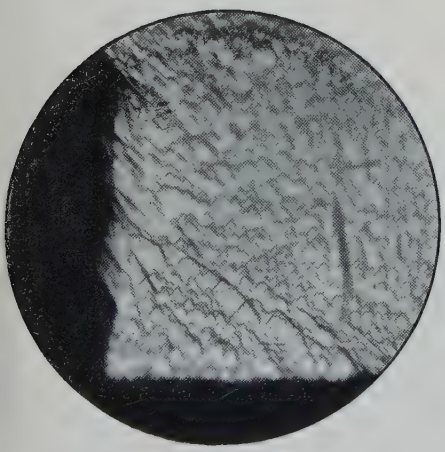

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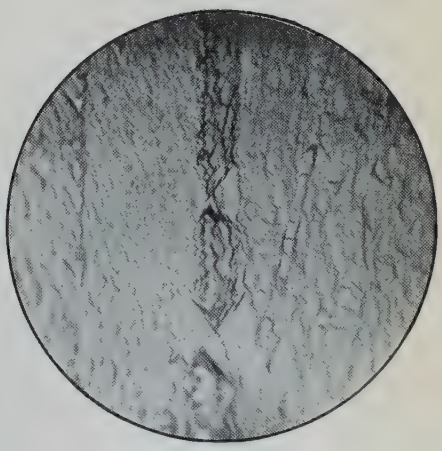
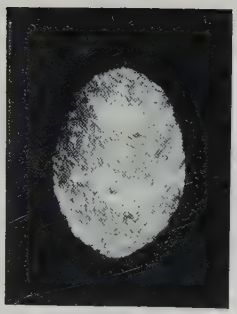


Fig. 29.

Fig. 3.



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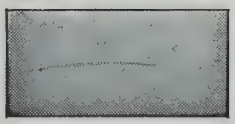
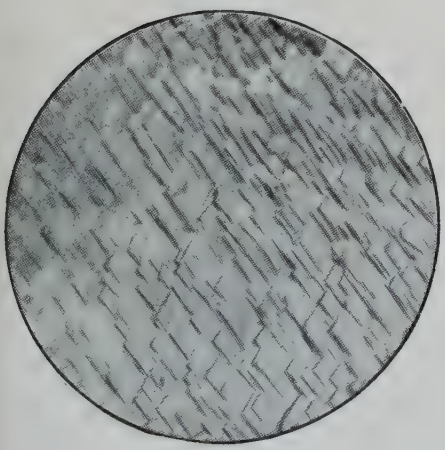


Fig. 10.

Fig. 14.

Fig. 15.



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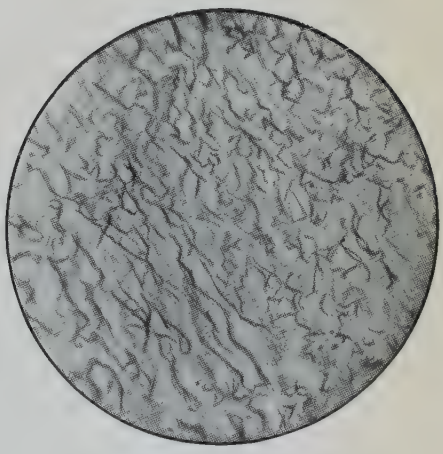

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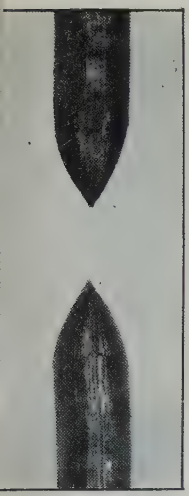

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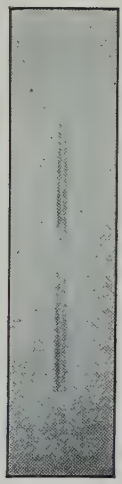
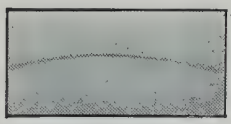


Fig. 27.

Fig. 19.

Fig. 20.



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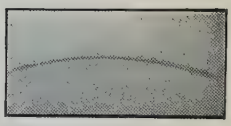

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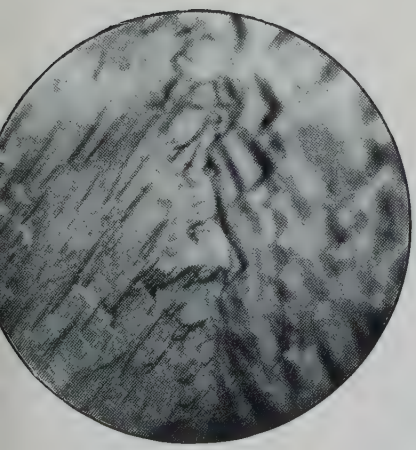
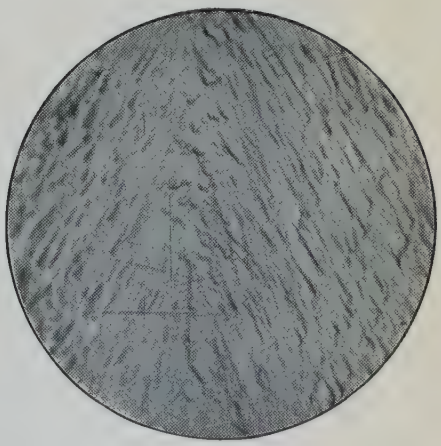


Fig. 33.



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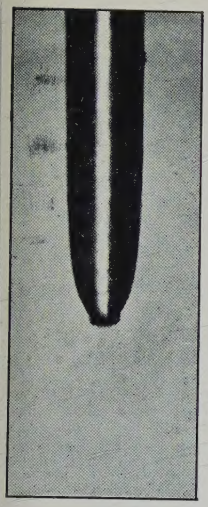
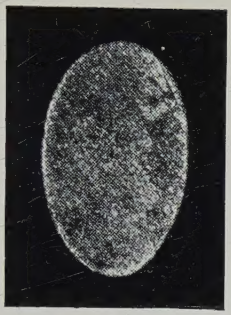


Fig. 17.

Fig. 28.



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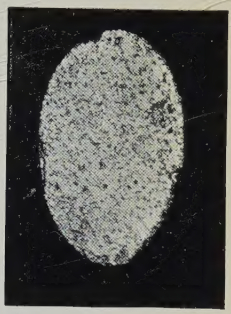
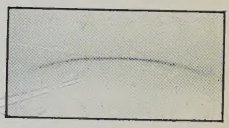


Fig. 22.

Fig. 25.



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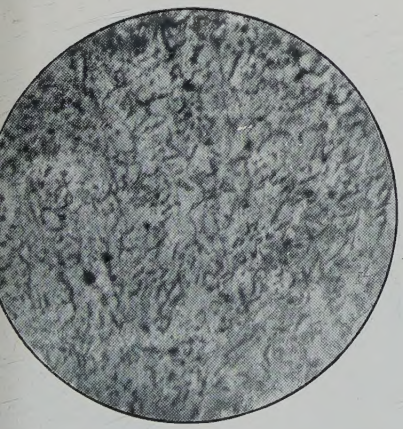

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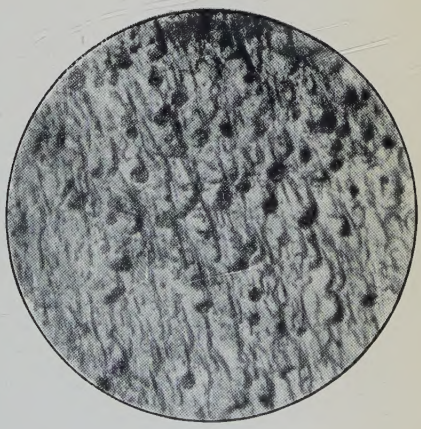

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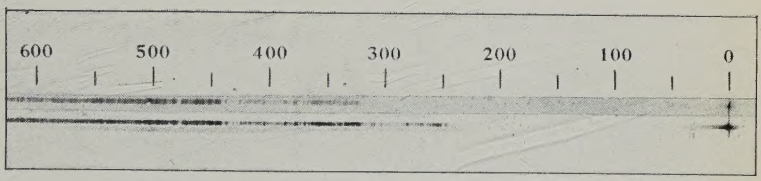
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